

Reaction Mechanisms of Fly Ash and Metakaolin Geopolymers and Environmental Compatibility

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Preface

This thesis is submitted to the Faculty of Civil Engineering at RWTH Aachen University for the degree of Doctor of Engineering (Dr.-Ing.). The research work was carried out at the Institute of Building Materials Research (ibac) at RWTH Aachen University, Germany. The supervisor is Professor Anya Vollpracht.

This thesis consists of an extended summary and six attached papers. Four of them constitute the core of this thesis, another two papers are outputs from collaborative research work with additional scientists and focus on specific applications of alkali activated binders. All papers are published in international scientific journals.

The author, Zengqing Sun, declares that the thesis and the work presented herein are his independent work and have been generated by him as the result of original research while in candidature for the degree of Dr.-Ing. at RWTH Aachen University. The thesis contains no material that was previously submitted for a degree at this university or any other institution.

Zengqing Sun

Aachen, 06 Jan. 2020

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I want to thank all my dear colleagues from the institute for supporting my work and creating pleasant working environment. In particular, I would like to thank my colleagues in the working groups 'Environmental Compatibility of Building Materials' and 'Binders' for the many fruitful discussions and expertise. Also many thanks for the colleagues in Binder Laboratory, Chemistry Laboratory, and Structure Laboratory for the kind support.

And last but not least, I want to express my deepest gratitude to my family and friends for all the direct and indirect support.

Abstract

Much is unknown about the reaction and environmental properties of geopolymers. In this work, the early age and long-term geopolymerization were studied, as well as the partitioning of main components, heavy metals and trace elements between geopolymer binders and aqueous phase at different leaching scenarios. In terms of the early age geopolymerization, isothermal calorimeter and in-situ XRD were used to characterize the heat and mineral evolution of fly ash geopolymer (FAG) and metakaolin geopolymer (MKG). The results were compared to alkali activated binders (AAB) based on ground granulated blast-furnace slag (GGBS). Factors including activator concentration, liquid-to-solid ratio, and curing temperature were taken into consideration. FAG is more temperature dependent, with much higher activation energy than MKG and GGBS based AAB. The dissolution of reactive minerals contained by solid precursor and formation of new crystalline phases were rapid and took place during the initial dissolution period. In addition, XRD results were analysed using the partial or no known crystalline structure method to quantify the amorphous evolution, which was demonstrated to be powerful in quantifying early age geopolymerization.

The evolutions of mechanical and chemical properties of geopolymers were profoundly influenced by curing protocol. Initial heat treatment contributes to the strength development and zeolite formation, in particular for the FAG. Meanwhile, this also leads to slightly worse pore characteristics. During sample handling and aging, natural carbonation took place in two ways: adsorption and reaction of CO₂ with mobile alkalis on the one hand and with framework oxygen atoms of the aluminosilicate gels on the other hand.

The partitioning of chemical species (Na, K, Al, Si, Ca, Ba, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Ti, V, Zn, chloride and sulfate) between the solid and aqueous phase was characterized in a broad pH range (1-14). Chloride and sulfate are of virtually pH independent characteristic. The overall leaching of Na, K, Ca, Si, Al, Co, Cu and Ni can be classified as amphoteric leaching pattern, in which concentrations increase at acidic and alkaline conditions. In contrast, the leaching of Mg, Zn, Pb, Mn, Sr and Sb exhibits cationic pattern, the maxima concentration locates in acidic pH range and decrease as pH values increase. Oxyanionic pattern, with high releases taking place in extreme acidic conditions and natural pH, is found for the leaching of As, V, Mo, Cr

and Se from FAG and MKG. Geochemical modelling was carried out, which offers a novel insight into the assemblages of solubility controlling phases. Meanwhile, limited by the not fully known chemistry of geopolymer, the current geochemical modelling is far from satisfactory, which deserves further investigation.

The leaching of monolithic geopolymer mortars were conducted following the European specification CEN/TS 16637-2. Results show that the dynamic surface leaching of Na, K, Al, Si, Ca, Ba, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, chloride and sulfate is mainly controlled by diffusion, while surface wash-off, solubility and depletion also take place. A comparison with the leaching of cement based materials and the regulatory limits in Germany and in the Netherlands was conducted. Leaching of above heavy metals and trace elements (except B, V and Mo) from geopolymers are in a similar range as for cementitious binders. The cumulative releases of V are higher than for most cementitious materials but still meet the requirement in the Netherlands (in Germany there is no valid threshold to date). In addition, no changes in phase composition on the surface layer of geopolymers were observed after leaching.

The GGBS based AAB possesses superior compressive strength, polishing- and skid-resistant property, which can be used for the construction of pavement surface layer. The flexural strength of GGBS based AAB is higher than cement counterpart of the same strength grade, suggesting a higher capacity to withstand bending damage. Moreover, equivalent CO₂ emission of GGBS based AAB paving is around 40 % lower than its OPC counterpart. All these results indicate that GGBS based AAB can be used as an environmentally friendly pavement binder. Depending on the mix composition, the GGBS based AAB, MKG and their mixture synthesized in this thesis can be used to produce ambient temperature cured pervious concrete of high aggregate-to-binder ratio.

Content

Preface.....	I
Acknowledgement.....	II
Abstract.....	III
Content	V
List of papers.....	VI
Core publications	VI
Application oriented publications.....	VII
1 Introduction	1
2 Objectives, structure and limitations	2
2.1 Objectives of this thesis	2
2.2 Structure of this thesis.....	3
2.3 Limitations of this thesis	5
3 State of the art.....	5
3.1 General description of alkali activated binders	5
3.2 Geopolymer and geopolymerization.....	7
3.3 Application and commercialization of geopolymers	10
3.4 Environmental properties of geopolymer	13
4 Discussion of main findings and conclusions.....	14
4.1 Early age geopolymerization characteristics	14
4.2 Long-term geopolymerization characteristics	15
4.3 Partitioning of chemical components.....	16
4.4 Leaching of monolithic geopolymer mortars	17
4.5 Application of GGBS based AAB and geopolymers	18
5 Outlook.....	19
6 References.....	20

List of papers

Core publications

- I **Isothermal calorimetry and in-situ XRD study of the NaOH activated fly ash, metakaolin and slag**
Zengqing Sun; Anya Vollpracht
Cement and Concrete Research, Volume 103, January 2018, Pages 110-122
(<https://doi.org/10.1016/j.cemconres.2017.10.004>)

- II **One year geopolymerisation of sodium silicate activated fly ash and metakaolin geopolymers**
Zengqing Sun; Anya Vollpracht
Cement and Concrete Composites, Volume 95, January 2019, Pages 98-110
(<https://doi.org/10.1016/j.cemconcomp.2018.10.014>)

- III **pH dependent leaching characterization of major and trace elements from fly ash and metakaolin geopolymers**
Zengqing Sun; Anya Vollpracht; Hans A. van der Sloot
Cement and Concrete Research, Volume 125, November 2019, 105889
(<https://doi.org/10.1016/j.cemconres.2019.105889>)

- IV **Leaching of monolithic geopolymer mortars**
Zengqing Sun; Anya Vollpracht
Cement and Concrete Research, Volume 136, October 2020, 106161
(<https://doi.org/10.1016/j.cemconres.2020.106161>)

Application oriented publications

I Study of alkali activated slag as alternative pavement binder

Zengqing Sun; Xiaochen Lin; Pengfei Liu; Dawei Wang; Anya Vollpracht;
Markus Oeser
Construction and Building Materials, Volume 186, 20 October 2018, Pages
626-634
(<https://doi.org/10.1016/j.conbuildmat.2018.07.154>)

II Pervious concrete made of alkali activated slag and geopolymers

Zengqing Sun; Xiaochen Lin; Anya Vollpracht
Construction and Building Materials, Volume 189, 20 November 2018, Pages
797-803
(<https://doi.org/10.1016/j.conbuildmat.2018.09.067>)

1 Introduction

Cement concrete is the central to civil infrastructures that enables and improves the quality of life. The annual consumption of concrete is over 10 billion tonnes, making it the second most used commodity only after water [1]. However, the production of cement is associated with huge greenhouse gas emission, which stems from the high temperature calcination of raw materials and conversion of calcium carbonates to oxides [1]. An urgent need in developing and commercializing alternative construction materials is arising to balance the housing / infrastructure demands and sustainable development.

Geopolymer is one of the robust candidates, which possess excellent engineering properties and reduced environmental footprints. Fig. 1 depicts the yearly publications referenced in *Web of Science* with the keywords 'geopolymer'. It can be clearly seen that geopolymer has been attracting increasing attention in the 2000s and onwards. Materials extensively used for geopolymer synthesis are industrial wastes / by-products, which generally contain various amounts of toxic components. These components may be leached out when get contact with water, resulting in environmental contamination. To date, rarely attention has been paid to the environmental compatibility of geopolymer as construction materials.

In this work, geopolymers were synthesized using fly ash (FA) and metakaolin (MK) as solid precursors. Apart from characterizing the reaction properties and strength development of obtained geopolymers, the binding and leaching properties of Na, K, Al, Si, Ca, Ba, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Tl, V, Zn, chloride and sulfate were studied.

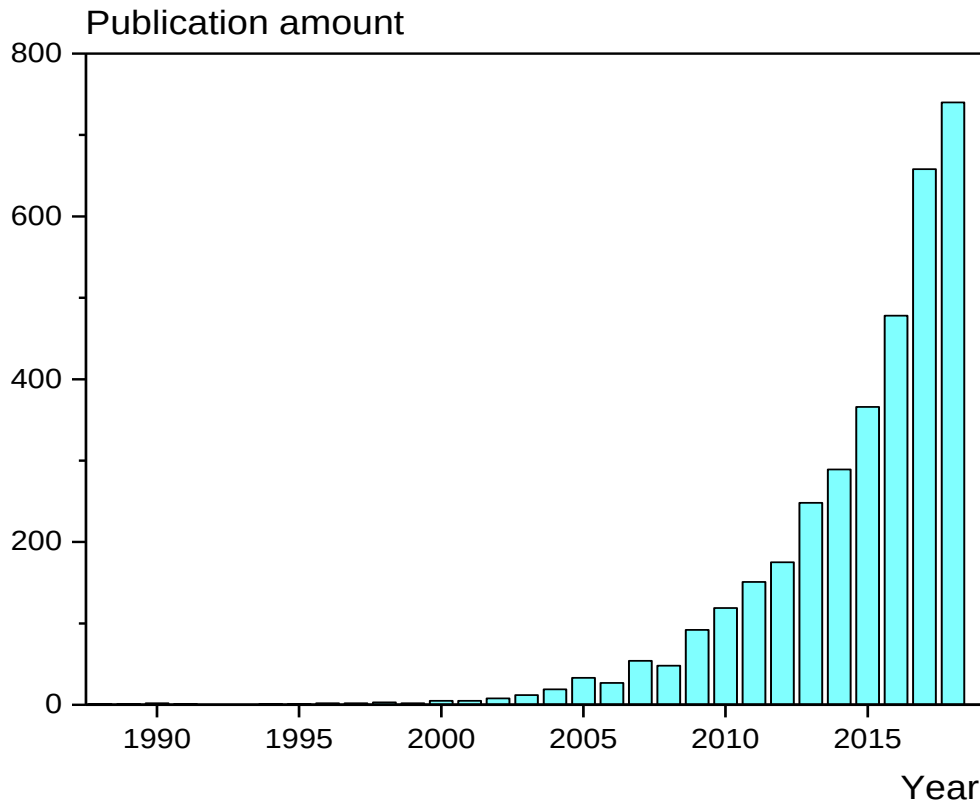


Fig. 1 Publications with keyword ‘geopolymer’ (data from Web of Science)

2 Objectives, structure and limitations

2.1 Objectives of this thesis

The aim of this thesis is to investigate the reactions and the leaching characteristics of fly ash geopolymer (FAG) and metakaolin geopolymer (MKG). To reach this aim, the main objectives are as follows:

- (1) Evaluating the reactivity of solid precursors, and synthesizing geopolymers with suitable mechanical properties for general engineering application scenarios.
- (2) Figuring out the influence of precursor reactivity, activator concentration, liquid-to-solid ratio, curing temperature on early age and long-term geopolymerization.
- (3) Revealing the partitioning of main components, heavy metals and trace elements between geopolymer binders and aqueous phase at different leaching scenarios.

2.2 Structure of this thesis

The structure of this thesis then includes state-of-the-art review of geopolymer, discussion of main findings and conclusions, followed by an outlook and six attached papers. The state-of-the-art section is composed of the existing knowledge on alkali activated binders (AABs), geopolymer and geopolymerization, application and commercialization of geopolymers, and environmental concerns about geopolymer based construction materials. Four of the attached papers constitute the core of this thesis, and another two papers are outputs from collaborative research work with additional scientists and focus on specific applications of AABs. All papers have been published in international scientific journals.

In Paper I [2], the early age reaction properties of FAG and MKG were quantitatively investigated. Reaction heat was *ab initio* documented, in which the influence of activator concentration, liquid-to-solid ratio, and temperature were considered. Given that the predominant role of amorphous phases in geopolymerization, the partial or no known crystalline structure (PONKCS) method was applied to characterize the amorphous evolution. Dissolution of raw materials and formation of reaction products are accompanied with heat change of the reaction system. A cross-check of quantitative XRD with isothermal calorimetry can help evaluate the reliability of the quantification method. The findings also provide information about the precursors and geopolymerization kinetics for followed work.

Paper II [3] characterizes the development of macro- and micro-properties of FAG and MKG in a time scale of one year. The synthesis and curing protocols significantly influence the initial reaction kinetics. The quality of reaction products is essential in determining the durability of obtained materials. A detailed characterization of pore size evolution, strength development, reaction products are helpful to fill the knowledge gap between material synthesis and durability of obtained geopolymers. Geopolymers used for further investigation were produced based on the findings from this work.

Paper III [4] investigates the partitioning of chemical components between aqueous and solid phases. For which, FAG and MKG mortars were leached in a broad pH range (1-14). The leaching behaviours of major components, heavy metal and trace elements were revealed. In addition, leaching characteristics of framework elements are coupled with geochemical modelling, which offers knowledge on the assemblages of solubility controlling phases and might bring new insight into the

environmental aspect analysis of geopolymers. It should be pointed out that Zengqing Sun designed and performed the experiments, analysed the data, drafted the manuscript; Prof. Anya Vollpracht directed and supervised the work; Dr. Hans A. van der Sloot aided in proofreading the results of the thermodynamic modelling as a supervisor for this specific topic. All authors discussed the results and commented on the manuscript.

Paper IV [5] assess the leaching of monolithic geopolymers in order to evaluate the environmental compatibility. Leaching of chemical components from geopolymer mortars was conducted. Apart from characterizing the leaching behaviours of main components, heavy metals and trace elements, the obtained leaching data were compared with cement-based materials to figure out the relative environmental impacts. Factors controlling the leaching process were analysed using different methods, which can afford insights in stabilizing of problematic components.

Beyond the above investigations focusing on reaction and leaching of geopolymers, two application-oriented studies of AABs (including geopolymers) were also covered by this thesis. In ‘Study of alkali activated slag as alternative pavement binder’ [6], a clinker-free cementitious binder for heavy duty concrete pavement was synthesized through an alkali activation of ground granulated blast furnace slag. The suitability of synthesized GGBS based AAB as alternative pavement binder, including flexural and compressive strength, anti-polishing property and skid resistance, was characterized and compared with OPC counterpart. Moreover, the equivalent CO₂ emission was calculated. Several researchers contributed to this publication, in detail, Zengqing Sun, Dr. Xiaochen Lin, and Prof. Dawei Wang conceived of the presented idea; Zengqing Sun prepared all specimen, performed the setting time tests, reaction and mechanical property measurements, equivalent CO₂ emission calculation, and wrote the manuscript; Dr. Pengfei Liu carried out the polishing and skid resistance characterization; Prof. Anya Vollpracht and Prof. Markus Oeser directed and supervised the work.

In the second study, ‘Pervious concrete made of alkali activated slag and geopolymers’ [7], GGBS based AAB and geopolymer binders were developed for application as pervious concrete pavement. Properties of compressive strength, density, total porosity and water permeability were fully studied. Both studies gained confidence for the field application of AABs as an environmentally friendly alternative binder. This work was designed by Zengqing Sun and Dr. Xiaochen Lin; operated

and manuscript drafted by Zengqing Sun; directed and manuscript reviewed by Prof. Anya Vollpracht. All authors provided critical feedback and helped shape the research, data analysis and manuscript.

2.3 Limitations of this thesis

Geopolymers are inherent considerable complex in constituents and reaction process. The studies presented in this thesis are limited concerning binder types and leaching protocols. Solid precursors used for geopolymer are commercial FA and MK, emerging precursors for example calcined clays of lower quality made from other clay minerals rather than kaolin were not covered. Geopolymer mortars were produced for mechanical property and environmental compatibility evaluation, in which only standard sand with a maximum size of 2 mm was used as aggregate. The binding property of heavy metals and trace elements might depend on geopolymerization age. All leaching shown in this thesis are based on hardened geopolymers without taking fresh and recycled geopolymers into consideration.

3 State of the art

3.1 General description of alkali activated binders

AABs refer to a broad binder system obtained via the reaction of alkali source with solid precursors [1, 8]. Activators can be solid or aqueous alkali hydroxide, silicate, sulfate, carbonate, aluminate, and their mixtures [2, 9]. Solid precursors are normally silicate-bearing, which comprise conventional clinkers, natural pozzolans, metallurgical slags, combustion ashes, calcined clays and other artificially synthesized aluminosilicates / calcium (alumino)silicates [9, 10]. On the basis of reaction mechanism and chemistry of main reaction products, AABs are generally classified into two subsets (as shown in Fig. 2), i.e. high-calcium system (with the representative of GGBS based AAB) and low-calcium system (also known as geopolymer, detailed description will be given in section 3.2) [1, 8]. Numerous studies have demonstrated that AABs produced under well-tailored mix design and curing procedure possess beneficial properties such as high early and final mechanical strength, thermal resistance, stability under chemical attack, strong adhesion to different surfaces, etc. [1, 8, 11, 12]. In addition, the estimated CO₂ saving characteristic of AABs can be up to 97 % in comparison with Portland cement [8, 12].

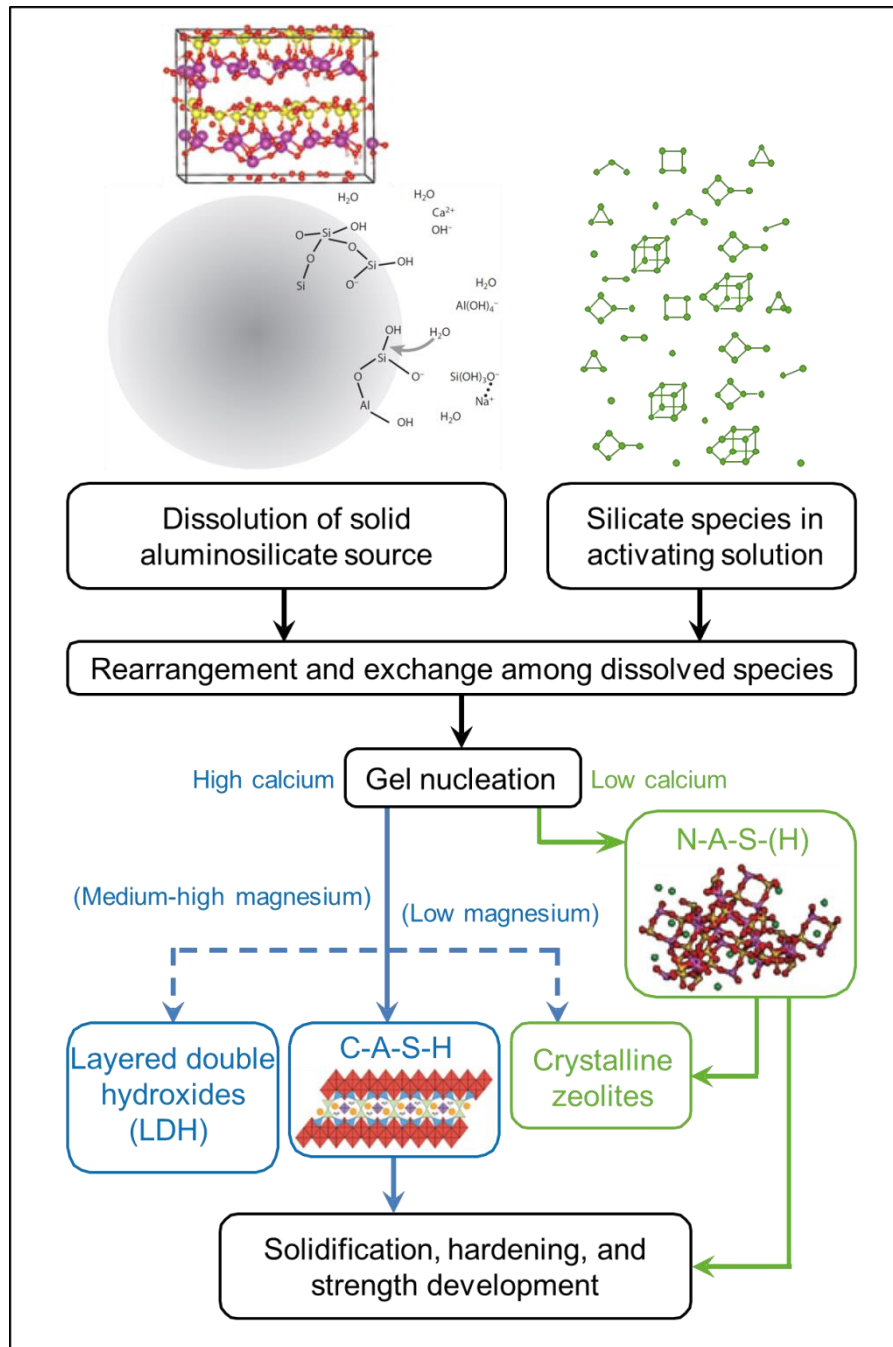


Fig. 2 Schematic illustration on reaction processes and products of AABs [1]
(The left-hand pathway represents the reactions of high-calcium systems, in which the content of magnesium influences the nature of secondary products. The reactions of low-calcium content are depicted in the right-hand pathway)

History about AABs can be dated back to the early 1900s, when Kühl patented studies on mixtures of blast furnace slag with alkaline components as ‘developing material’ that provides performance ‘fully equal to the best Portland cements’ [13]. Detailed scientific investigations on these binders were conducted by Purdon in the 1940s [14]. The findings were then commercialized in the 1950s in Belgium. Around

the same period or later, the former Soviet Union scientist Glukhovskiy developed binders via the alkali activation of low-calcium or calcium-free aluminosilicates [15], and successfully utilized the obtained materials in infrastructure and domestic constructions [16]. Studies and applications of AABs have also been reported in Northern Europe, China, United States, etc. [17-19]. One of the milestones that should be mentioned is that Davidovits developed and patented several aluminosilicate-based formulations in the 1970s in France [20]. Since then the terminology 'geopolymer' has been widely used.

3.2 Geopolymer and geopolymerization

As aforementioned, AABs can be further classified into different subclasses. From this section onwards, attention is focused on the low-calcium AABs, i.e. geopolymer. Though chemically bonded phosphate ceramics are also defined as geopolymer [21, 22], this particular group is not covered by this work.

Currently, siliceous FA and MK are the most frequently used solid precursors for geopolymer synthesis [8, 9]. FA is the fine particulate residue of coal combustion and a typical by-product of coal-fired power plant. FA particles are driven out of the boiler furnace together with the flue gases and captured by electrostatic precipitators or other methods in chimneys. Ashes that fall to the furnace bottom are called bottom ash. Physically, FA particles are very fine and close to spherical. In chemistry, FA is highly vitreous and composed of incombustible minerals initially from coal. Benefiting from its favourable physicochemical properties, FA has been widely used as supplementary cementitious material (SCM) in concrete.

MK is the thermal treated product of kaolinitic clays at temperatures of about 500-800 °C. In comparison with original kaolin, MK remains the layered clay structure, but is disordered and partially dehydroxylated [9]. In addition, thermal treatment makes aluminium readily available because of the formation of energetic Al-O-Al bonds [8]. All these make MK suitable as solid precursor for geopolymer synthesis.

Other industrial by-products or municipal wastes, such as red mud, catalyst residues, rice husk ash, waste glass, waste ceramic, etc., have been developed as precursors. Recent studies about geopolymers produced using these new precursors are well reviewed in [10]. Physicochemical properties of most widely used activators (sodium hydroxide, sodium silicate) as well as other typical activators are well documented in literature [1, 8, 9].

Geopolymerization is an integrated reaction process that converts precursors and activators to geopolymeric materials. Glukhovsky [15] first proposed a conceptual model for the alkali activation of materials mainly composed of reactive silica and alumina. The model was then elaborated on and extended by other researchers [11]. In the modified model, geopolymerization is simplified into following steps: breaking down of solid precursors under alkaline attack and release of reactive Si and Al; reorientation and gelation of dissolved species; polymerization and condensation of gels [1, 8, 11, 12]. In detail, the amorphous aluminosilicates initially contained by solid precursor dissolve rapidly at high pH. A complex mixture containing aluminate, silicate, and aluminosilicate species is then formed. Solution gets supersaturated under the continuous dissolution of solid precursors, which promotes the gelation process. Formed gels then rearrange and reorganize to increase the connectivity of the gel networks. Geopolymers with a highly cross-linked aluminosilicate network are then formed [1, 8, 11, 12]. It should be mentioned that these reaction processes are highly coupled and take place concurrently. And the time required for supersaturation is significantly influenced by mix design and synthesis procedures. In some cases, the concentration of dissolved ions remains far from saturation and gelation will not occur [11].

Fernandez-Jimenez et al. [23] provided a graphic description (Fig. 3) about the microstructure development of FAG, which offers direct view into the reaction process. The contact areas on the surface of FA particles gradually dissolve under the chemical attack of alkaline activator. This leads to the exposure of the inner sides of FA particles as well as the smaller particles initially enclosed by larger ones (if any). With the diffusion of activator, dissolution of FA takes place both from the outside and from the inside. Reaction products are also simultaneously generated from both sides. Meanwhile, massive precipitation of reaction products may cover the unreacted parts as a crust that hinders further dissolution. Differences between FAG and metakaolin geopolymer (MKG) have been reported in [24]. According to White et al. [24], the dissolution of alumina and silica from the layered sheets of MK may result in the exfoliation of the MK structure to some extent. Hence, more layers are exposed for further geopolymerization.

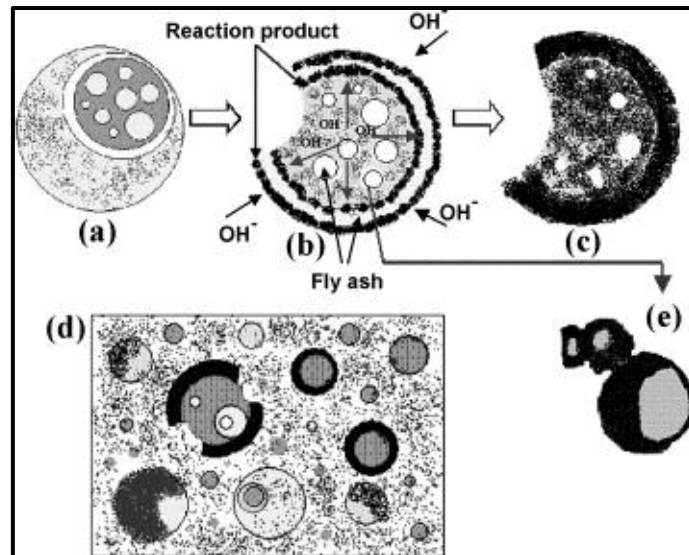


Fig. 3 Descriptive model of reaction of FAG [23]

The main reaction product is a type of alkali aluminosilicate gel, which is often represented as N-A-S-(H). N-A-S-(H) is highly cross-linked but structurally disordered, silicon and aluminium are of tetrahedral coordination [25, 26]. According to Duxson et al. [26], substitution of silicon by aluminium takes place, and the associated negative charges are balanced by alkali cations. In addition, sodium can be substituted by potassium or calcium, resulting in a more complex gel structure N,K-(C)-A-S-(H) [8]. Fig. 4 depicts the schematic structural features N-A-S-(H).

Over decades, efforts have been made in revealing the structural model of geopolymer. Davidovits [27] proposed an amorphous hydrated zeolitic leucite structure for potassium activated MKG. The hypothesis is supported by Bell et al. [28] via X-Ray pair distribution function analysis (PDF) of a MKG. The X-ray PDF method involves the collection of X-ray data in total scattering experiments, correction for experimental effects (geometry and background of the detector), and Fourier transformation [29]. Considerable promise has been shown by X-ray PDF method in examining both short range (2-5 Å) and medium range (5-20 Å) structure of amorphous and nanocrystalline materials [30, 31]. Considering the similarity between geopolymer and zeolite in processing and coordination states of framework components, Provis et al. [25] stated that the gel is fundamentally zeolite-like, but lacks long-range crystalline order in chemical sense. Meanwhile, changes of gel structure and composition over time have been reported by Fernandez-Jimenez et al. [32] and White et al. [24], respectively. This increases the difficulty in revealing the structural model.

Secondary reaction products are frequently detected in geopolymers, particularly those synthesized using hydroxide activators. For example, zeolite A and X, low-silica faujasites are often identified in MKG, with chabazite, sodalite and cancrinite phases being typical in FAG systems [33-35].

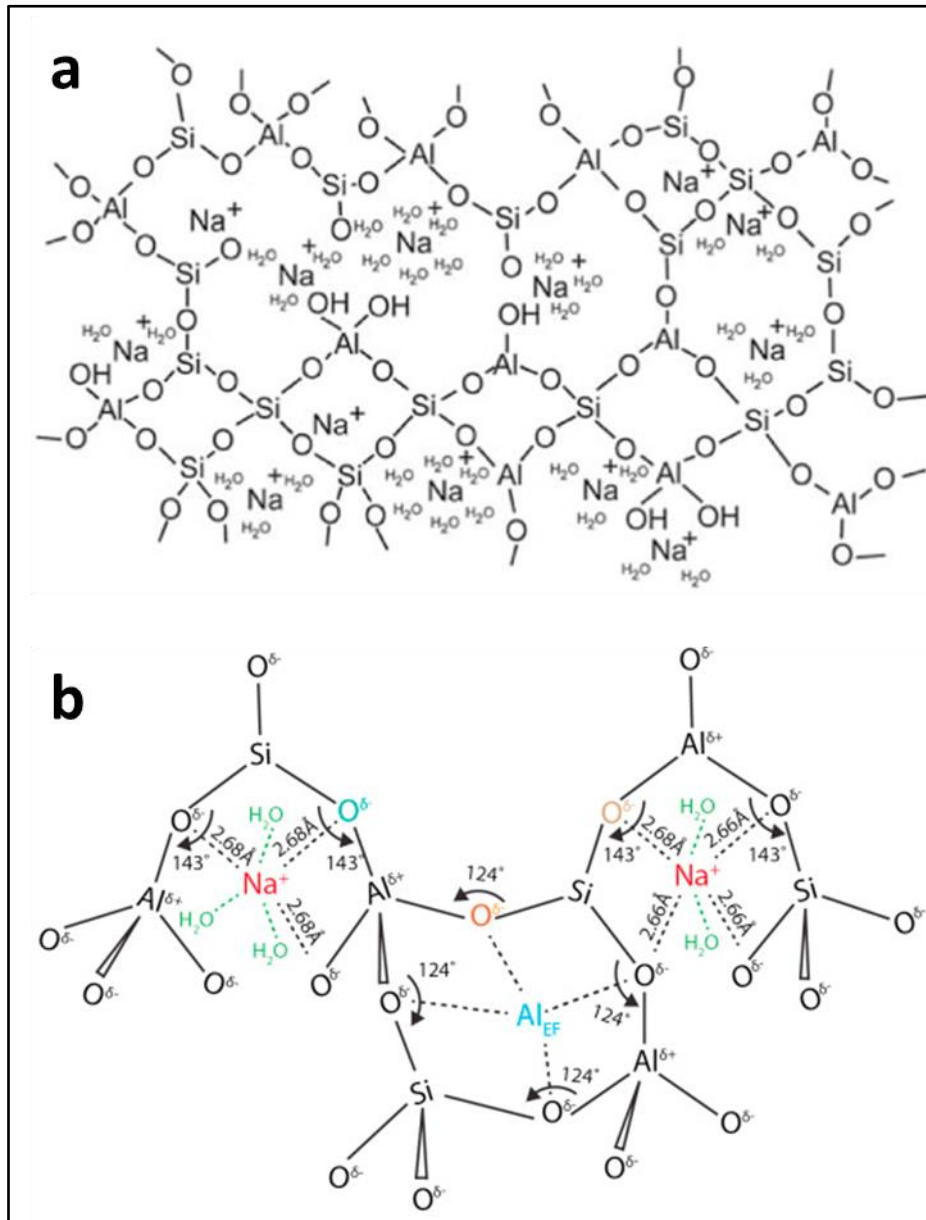


Fig. 4 Schematic structures of N-A-S(H): (a) adapted from [34], (b) adapted from [35]

3.3 Application and commercialization of geopolymers

Extensive studies have been conducted to investigate the short- and long-term engineering properties of geopolymer. Provis et al. [8, 12] summarized that geopolymer concrete possesses excellent compressive strength and sulfate

resistance over cement concrete, low creep, low permeability and little drying shrinkage [8, 12]. Pyrament cement, a brand patented by Davidovits in the 1980s, is one of the first commercialized geopolymer materials. This material was soon adopted for the construction of industrial pavements, highway roads, and aircraft runways in the US [36]. These constructions showed very good working conditions after many years in service [36]. In 2013, a 4-story building comprising suspended geopolymer concrete floors was put into service in Queensland [37]. One year later, the Brisbane West Wellcamp Airport (BWWA), built with approximately 40,000 m³ of geopolymer concrete, was opened for business [38]. Moreover, geopolymer can be used in aggressive environments. Geopolymer was demonstrated to meet the most demanding German standard for corrosion resistance, and can be used for the repair and rehabilitation of sewer infrastructures [39]. More and more companies have been founded that manufacture and supply geopolymer materials [40]. These applications and commercialization practices generate confidence in geopolymer concrete.



Fig. 5 Application examples of geopolymer concrete: (a) precast panels [37], (b) retaining wall surrounding a bridge [1], (c) residential housing slab [1], (d) in-situ cast aircraft pavement [38]

In addition to the application in infrastructure construction, geopolymer has been considered as immobilization matrix of hazardous / nuclear wastes [8]. Efforts have been made in using the geopolymer technology to solidify / stabilise toxic species. The immobilization process on heavy metals is complex and involves physical adsorption, encapsulation of contaminants, chemical fixation, etc. [12, 41-43]. The immobilization of copper (Cu) by geopolymer is good but not uniformly outstanding, which is generally attributed to its smaller radius and therefore reduced tendency to be trapped in nano-pore networks [12]. In the case of Pb(II), formation of Pb-silicate compounds of very low solubility contributes to the binding [41, 42]. In addition, lead was also reported to possess the capacity in modifying the pore structure of geopolymer. Arsenic (As) prefers to associate with iron-rich regions derived from FA [44]. To date, the immobilization of cadmium (Cd) by geopolymer has not been as successful as in OPC matrices. Cd is chemically immobilized during OPC hydration by substitution of Cd on calcium sites to form Ca/Cd-silicate hydrate gels [45]. Due to the low solubility of $\text{Cd}(\text{OH})_2$ in near-neutral and elevated pH, the highly alkaline pore solution is regarded as the most likely host phase of cadmium in geopolymer [46, 47]. It is hypothesized in some studies that Zn(II), Cu(II), Cd(II) and Cr(III) can replace the alkali cations in balancing the negative charge originated from the substitution of silicon by aluminium [48, 49]. This hypothesis was somehow excluded by the findings in [43, 50] that decreased leaching of alkali ions from geopolymer was detected after incorporating heavy metals. However, the findings reported in [43, 50] cannot be considered absolutely conclusive since the leaching behaviours were evaluated via simply measuring eluate conductivity. Formation of coordination bonds between the non-bridging Si-O / Al-O end members and heavy metals ions have been proposed [50]. Notably, the identification was merely based on the qualitative evidences from FTIR measurement and in-depth investigation is required.

The stabilization behaviour also depends on chemical properties of compounds containing toxic elements. For example, PbS added in geopolymer matrix was observed to be segregated from the binder, which is assigned to its inert characteristic to alkaline condition [51]. When added in soluble form (e. g. PbO , PbSO_4), Pb was found to be dispersed throughout the matrix and chemically bound [51]. Meanwhile, soluble Cr(VI)-bearing salt (e.g. Na_2CrO_4) incorporated in geopolymer matrix is normally highly leachable [52, 53]. A conversion of Cr(VI) to

less toxic and less mobile Cr(III) is proposed, for which ferrous compounds or sodium sulphide (Na_2S) can be applied.

The usefulness of geopolymers for immobilization of low-level and intermediate-level nuclear waste has been tested. Geopolymer showed better immobilization property for some problematic elements (for example caesium (Cs)) than OPC immobilization [12]. Cs appears to be chemically bound as a charge-balancing cation in geopolymer structure [54]. In addition, advantages of geopolymer over OPC include minimal production of radiolytic hydrogen during dewatering, lack of freeze-thaw problems, thermal and chemical resistance [55].

3.4 Environmental properties of geopolymer

To date, studies about the environmental properties of geopolymer focus either on the life cycle environment impact assessment (resource depletion, global warming potential, etc.) or on the suitability in waste immobilization. Compared with Portland cement, reduced CO_2 emissions of geopolymer have been extensively reported [8, 9, 12]. The reduction, ranging from 9 % to 97 %, is determined by binder mix design, synthesis and curing procedure, composition of the reference cement, geographical parameters, etc. For example, the resource-intensive production of MK makes it less environment-friendly than FA. Activators, both hydroxide and silicate based, cause significant contribution to global warming potential [12]. These findings help to optimise the production of geopolymer materials.

The property of geopolymer in waste solidification has been discussed above. Laboratory leaching has been conducted among these reported studies, but all these studies focus on the leaching of artificially supplied toxic elements [44, 47, 56-58]. In addition, different from being used as construction and building materials, cementitious matrixes solidifying hazardous materials are meant to be deposited and the corresponding release limits are much higher.

The environmental impact in terms of leaching of heavy metals and trace elements from geopolymers designed for construction application has not been reported. It should be mentioned that the industrial wastes or by-products extensively used for geopolymer synthesis contain different amounts of toxic elements. As a part of the quality surveillance of FA in our institute, over 300 FA samples from different power plants in Germany were tested for the heavy metal and trace element content. Fig. 6 shows the statistic results of selected elements. Compared with the average content

of cement [59], FA normally contains higher contents of heavy metals and trace elements. This indicates that geopolymers synthesized using these wastes / by-products possess the potential of bringing contaminations into the environment. An urgent need is arising to assess the environmental compatibility and to reveal the leaching behaviours of heavy metals and trace elements from geopolymers.

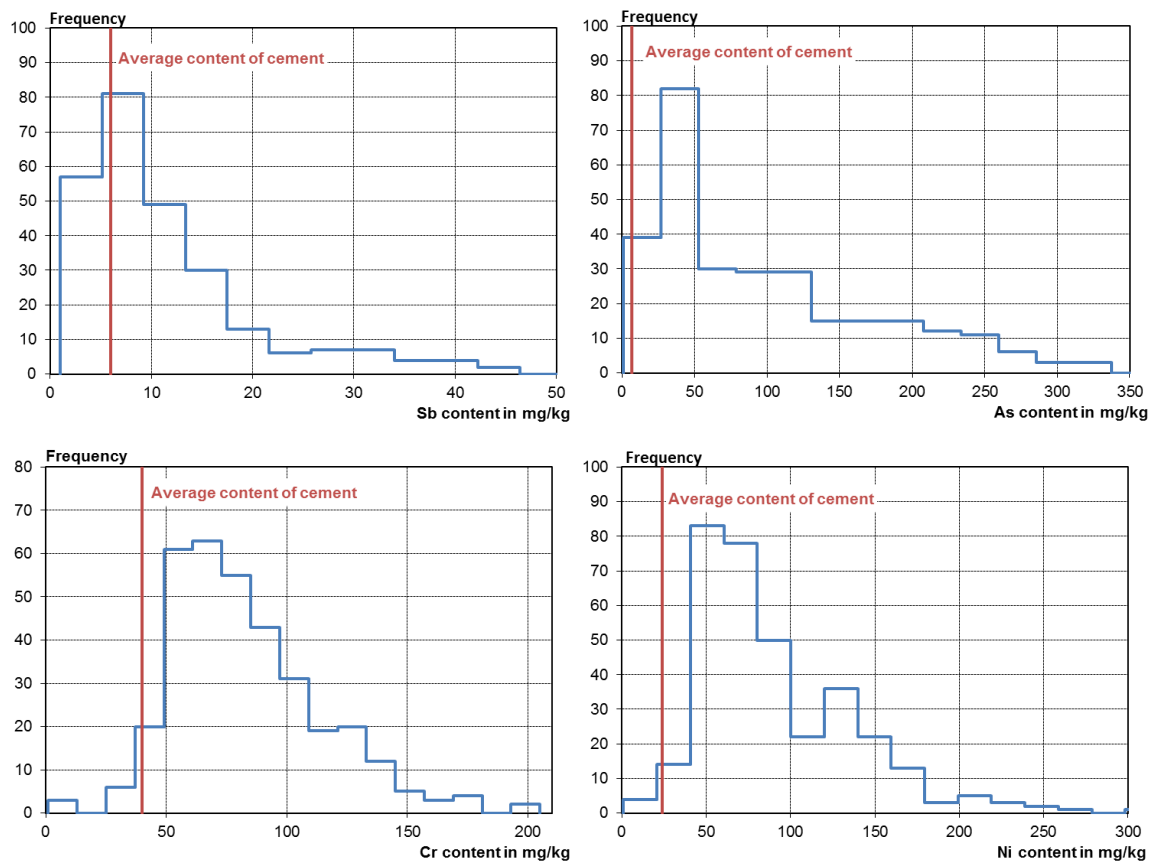


Fig. 6 Statistic results of Sb, As, Cr and Ni content in fly ashes in Germany

4 Discussion of main findings and conclusions

4.1 Early age geopolymerization characteristics

The geopolymerization process is determined by precursor reactivity, activator type and concentration, liquid-to-solid ratio, and temperature. At 20 °C, FAG showed a single exothermic heat response, no other remarkable heat features can be found even with increased activator concentration or prolonged reaction time. In contrast, the initial dissolution peak of MKG was followed by a short dormant period and another broad exothermic peak. The dormant period, entitled as induction period in cement hydration, is supposed to be the time needed for the growing up of

concentration [16]. The polymerization and condensation processes are exothermic and make the main contribution to the second peak [60]. Activator concentration possesses bilateral influences on reaction of NaOH activated MK at ambient temperature. On one hand, higher concentration involuntarily accelerates the dissolution by supplying more OH^- and shortens the induction period [9, 61]. On the other hand, the fast precipitation of reaction products on surface of precursor grains might affect the diffusion of dissolved ions through reaction product layer for further gelation and polymerization [23, 62]. In the concentration range used in this study (6-12 mol / L), the increase in activator concentration extends the duration of the second peak.

An optimal liquid-to-solid ratio can be inferred from the calorimetry curves, low liquid-to-solid ratio retards the reaction because insufficient OH^- , whilst water content is escalated when high liquid-to-solid ratio is applied. The influence of temperature is more critical especially for FAG. Increasing temperature distinctly converts the single exothermic heat response of NaOH activated FA at temperature into multiple-peak system. The cumulative heat release within 72 h at 30 °C and 40 °C is 2.6 and 5.4 times of that at 20 °C, respectively, both are much higher than its MK counterpart. In addition, the corresponding activation energy of 9 mol / L NaOH activated FA and MK is 85.5 ± 4.6 kJ/mol and 46.3 ± 2.4 kJ/mol. Apart from the predominant reaction product of N-A-S-(H), secondary product (cancrinite) was detected in NaOH activated FA. The formation of cancrinite was rapid and took place during the initial dissolution phase indicated by the first calorimetric peak. When putting the quantified results from PONKCS method together with the reaction heat evolution, a well correlation can be achieved, demonstrating that the PONKCS can be used to obtain reasonably accurate and meaningful quantification result of geopolymerization.

4.2 Long-term geopolymerization characteristics

The initial curing protocols, derived from isothermal heat release property, possess considerable effects on long-term reaction and mechanical property of geopolymers. Heat treatment is in particular beneficial for early age mechanical strength development of FAG. The strength improvement at early stage is influenced not only by temperature but also by the duration of heat treatment. For example, FAG specimen cured at 60 °C showed the best early age mechanical properties, sequentially followed by those cured at 40 °C, 30 °C and 20 °C. The 3 d compressive

strength of FAG cured at 60 °C for 12 h and 24 h are 8.8 and 13.5 times of counterparts initially cured at 20 °C, respectively. The significant enhancement is attributed to the minute reaction degree of FAG at ambient temperature because of low reactivity. Treatment at elevated temperature is necessary to overcome the energy barrier [63, 64]. With the extending of aging time, the strength of FAG initially cured at elevated temperatures gradually increased to reach maximum. In contrast, specimen originally cured at 20 °C showed high flexural and compressive strength after 96 days, with the one year flexural and compressive strength being 10.9 MPa and 71.4 MPa, respectively. Owing to the high reactivity property of MK, the influence of heat treatment on strength evolution of MKG is less pronounced. Apart from accelerated geopolymerization, rapid formation of zeolite phases were detected from FAG and MKG samples initially cured at elevated temperatures.

The microstructure was characterized by measuring the pore structure of geopolymer mortars using mercury intrusion porosimetry (MIP). The pore structures of MKG and heat treated FAG are almost built at early age because the rapid formation of hardened structure. In comparison, FAG specimen originally cured at ambient temperature showed lower porosity and the pores were of smaller median radius than counterparts initially cured at elevated temperatures. This is attributed to the gradual formation and growth of reaction products that fill large voids [23]. Natural carbonation of geopolymers were found, which are caused by the adsorption and reaction of geopolymers with CO₂ during sampling handling and aging. The carbonation can be divided into two groups: reaction of CO₂ with mobile alkalis and / or framework oxygen atoms in geopolymers. The former process is predominant at early age while the latter takes place slowly during aging.

4.3 Partitioning of chemical components

The partitioning of chemical components (Cl⁻, SO₄²⁻, Na, K, Al, Si, Ca, Mg, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, V, Zn) between the solid and aqueous phases in pH dependence leaching tests vary significantly. Chloride and sulfate show virtually pH independent characteristics, while the others exhibit pH dependent features including amphoteric, cationic and oxyanionic patterns. 70-80 % of chloride and sulfate are leached from FAG and MKG, which indicates that both components are mainly present in readily soluble species. The leaching of Na, K, Ca, Si, Al, Co, Cu and Ni exhibits amphoteric leaching behaviour, in which concentrations increase

at acidic and alkaline conditions. The minimum releases of Na, K, and Ca are obtained at material's natural pH. Notably, the leaching of Na and K from cement system is not strongly influenced by pH [65-68]. The difference can be attributed to the charge balancing role of Na and K in geopolymers. Moreover, the leached ratio of K from both geopolymers are similar while Na not, indicating K and Na may exist in different forms in geopolymers. As reported, Na^+ is more likely to form inner surface complexes with tetrahedral charge sites in aluminosilicate phases than K^+ [69-71]. The minimum leaching of Si from both geopolymers takes places around pH = 10, while the lowest aluminum concentrations are measured at pH around 5. The formation of $\text{Al}(\text{OH})_3$ might be responsible for the low content of Al in eluate at this pH range. The overall leaching of Mg, Zn, Pb, Mn, Sr and Sb can be classified as cationic pattern, the maxima concentration locates in acidic pH range and decrease as pH values increase. Oxyanionic pattern is found for the leaching of As, V, Mo, Cr and Se from FAG and MKG. In this case, the high releases take place in extreme acidic conditions and natural pH. The minima concentration normally locates at pH 4-6. Higher pH values than natural pH also result in concentration decrease. Since the chemistry of geopolymers is not fully known and a lack of thermodynamic data for geopolymeric phases persists, uncertainties and unresolved issues exist in current geochemical modelling. Meanwhile, the results still offer novel insights into the contributions of specific species and the assemblages of solubility controlling phases.

4.4 Leaching of monolithic geopolymer mortars

Much higher amount of Na and Si are leached from FAG than MKG, even though that the MKG initially contains more Na and Si than FAG. The lower reaction degree of FAG is supposed to be responsible for this phenomenon. The MKG shows higher release of Al and K than FAG, which is attributed to the higher initial content of both elements in MKG. Similar leaching characteristics are found for the leaching of Cl^- and SO_4^{2-} from both geopolymers, i.e. the measured concentrations decrease with the sampling time and depletion is observed during the leaching. Low concentrations are measured for most of the studied heavy metals and trace elements. And the cumulative releases of As, B, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Tl and Zn from FAG and MKG are in the same range as for cement based materials [72].

Leaching mechanisms were analysed using the data analysis procedure introduced in CEN/TS 16637-2 [73] and comparison of the eluate concentration with pore

solution [74, 75]. Following the evaluation concept described in CEN/TS 16637-2, the leaching of Na, Al and Si from FAG and can be regarded as diffusion controlled, while Ca is classified as solubility controlled. Compared with the target value, the normalized concentrations of Al from both geopolymer and Si from MKG are much lower at early age while higher at the final stages. The leaching of Al from FAG is further classified as delayed release [76]. Van der Sloot et al. [76] assigned this phenomenon to solubility controlling phases at the surface of the sample that can limit the leaching in the initial stage of the test. In addition, solubility might be also involved in the leaching of Si from MKG and Al from FAG and MKG because the measured concentrations at later periods are close to the pH dependent test results. Leaching mechanisms of heavy metals and trace elements were also analysed. The leaching of V from both geopolymers and Zn from FAG meet the diffusion controlled pattern described in CEN/TS 16637-2. The leaching of Cu from FAG is controlled by diffusion and surface wash-off, while depletion was found for leaching of Cu from MKG.

4.5 Application of GGBS based AAB and geopolymers

Laboratory tests showed that the GGBS based AAB possess similar compressive strength, anti-polishing property and skid resistance as cement reference, which can be used for the construction of heavy duty concrete pavement. In addition, the GGBS based AAB is of higher flexural strength than the cement counterpart, suggesting a higher capacity to withstand bending damage. Owing to the fast development of mechanical properties, GGBS based AAB can contribute to minimize traffic control caused by construction. Apart from the engineering advantage, the equivalent CO₂ emission of GGBS based AAB is about 40 % lower than cement paving.

The GGBS based AAB, MKG and their mixture can be developed to produce pervious concrete of high aggregate-to-binder ratio. Pervious concretes produced using above binders exhibit higher mechanical properties and better water permeability than cement pervious concretes. Benefiting from the elimination of elevated temperature curing, pervious concretes produced in this work is more sustainable than current reported studies using other AABs. All these findings indicate that GGBS based AAB and geopolymers synthesized in this work possess the potential to be used as an environmentally friendly pavement binder.

5 Outlook

In addition to the abovementioned results and discussions, following efforts should be taken into consideration to deepen investigations on reaction and environmental compatibility of geopolymers.

(1) The in-situ XRD measurement combined with data analysis using PONKCS method has been demonstrated to be powerful in quantifying geopolymerization. Meanwhile, the application of this analysis protocol is limited to the first several hours of reaction, since further geopolymerization is not notable for XRD measurement. More advanced characterization (for example NMR) and computational simulation of geopolymerization is proposed. In addition, cross-check of results from different techniques is needed to optimise the quantitative analysis toolkit of geopolymerization.

(2) In terms of precursor, there is insufficient availability of FA in developed countries. Long distance transport is then accompanied by cost problems. Massive utilization of MK as construction material is limited by its high cost. Nowadays, the focus of international research has moved to calcined low-grade clays, which are worldwide available in abundant quantities and cost effective. The environmental compatibility of geopolymers produced using calcined clays deserves detailed investigation.

(3) The geochemical modelling offers a detailed insight into the contributions from specific species and the assemblages of solubility controlling phases. It should be mentioned that the modelling results of Si, Al, Ca, and Mg in this thesis were far from satisfactory because the chemistry of geopolymer is not fully known. With the progress in fundamental investigation on geopolymerization, uncertainties and unsolved questions would be overcome. Apart from optimising the modelling of main components, adequate geochemical modelling of the heavy metals and trace elements in geopolymers is expected.

(4) Both the pH dependent leaching and the dynamic surface leaching conducted in this thesis are performed on hardened geopolymers. When geopolymer concretes are cast in-situ, the material gets in contact with surrounding water during setting and hardening. The leaching of heavy metals and trace elements is supposed to be higher, due to the simultaneously dissolution of solid precursors. To reveal this, the leaching behaviours of fresh geopolymers should be characterized. In addition, after being marketed, geopolymer concrete will be used in a large-scale. And there will be an increasing amount of waste debris from destruction of geopolymer based

structures in the future. Construction and demolition waste (CDW) is one of the most important waste streams generated world wide. There is a high potential of recycling and reusing CDW, for example, aggregates derived from CDW waste have been used in roads, drainage and other construction projects. To minimize environmental risks, it is necessary to investigate the leaching of geopolymeric CDW before reusing.

6 References

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Isothermal calorimetry and in-situ XRD study of the NaOH activated fly ash, metakaolin and slag

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ABSTRACT

Much is unknown about the reaction processes responsible for the formation and polycondensation of geopolymers and other alkali activated materials. In this work, isothermal calorimeter and in-situ XRD were adopted to study the heat and mineral evolution of NaOH activated fly ash, metakaolin and ground granulated blast furnace slag. Both activator concentration and temperature have profound influences on duration of exothermal geopolymerization peaks. NaOH activated fly ash is more temperature dependable, with much higher activation energy than metakaolin and slag. The dissolution of source precursor is rapid and the formation of new phases can be detected by the end of the initial dissolution period. The in-situ XRD measurement together with the POKCS analysis method promotes quantitative estimation of amorphous evolution during alkali activation.

1. Introduction

With a consummation of over 10 billion tonnes per year, concrete is the second most used commodity. Worldwide application of cement and concrete contributes to the modern civilization but introduces ~8% of global CO₂ emissions at the same time [1]. An urgent need is arising for the development and commercialization of environmentally friendly binders. Previous studies showed that alkali activated material (AAM), including those classified as geopolymers, possess properties including high compressive strength, acid and fire resistance [2,3]. Due to its comparable performances to traditional cementitious binders but with significantly reduced CO₂ emission, AAM is among the most widely researched alternative binders for construction [1–3].

The most extensively used solid source materials to produce AAM are fly ash (FA), metakaolin (MK) and ground granulated blast furnace slag (GGBS), with sodium hydroxide, sodium silicate and their mixtures as the most commonly used alkali activators [1,4]. Alkali activation of FA and MK results in the formation of so called geopolymers, which are drawing attention from academic and industrial fields. Extensive studies have been carried out to understand the complex reaction process in which the aluminosilicates precursors are converted into cementitious materials [3,5]. This multistep process is described as the dissolution of reactive Si and Al atoms from solid precursors, reorientation and gelation of dissolved species, followed by polymerization and condensation [1,2,5]. Duxson et al. [6] investigated the coordination and short-range ordering of silicon and aluminium in geopolymer gels. Results showed that substitution of silicon by aluminium can happen

within the gel framework, while the associated negative charge is balanced by alkali cations. This disordered gel shares the nanostructural features of zeolites in chemical sense, but lacks long-range crystalline order [1].

In contrast, the reaction products of alkali activated GGBS are primarily calcium aluminosilicate hydrates (C-A-S-H phases) [1]. A study from Puertas et al. [7] demonstrated that the C-A-S-H phases formed in alkali activated slag pastes exhibit compositional and structural differences from the C-S-H formed in OPC hydration. C-A-S-H is generally regarded as aluminium substituted C-S-H, in which Al³⁺ mainly exists in tetrahedral bridging sites within the silicate chains [1,7].

Each of these reactions corresponding to geopolymerization and alkali activation of GGBS occurs at a rate that is determined by several parameters, such as the nature of the solid materials, concentration and dosage of alkali activators, temperature, etc. [2,5,8]. In addition, all the reactions may occur in combinations, in series or in parallel [5,9,10]. Even though a complete understanding of all involved reactions seems to be unachievable, detailed researches related to reaction kinetics and products formation are essential not only to better understand the mechanism, but also to tailor AAMs for specific applications.

Given the complexity of the gel formation and its dependence on several compositional and processing parameters, various state-of-the-art technologies have been applied to investigate the early stage reaction behaviours. In-situ neutron pair distribution function (PDF) and density functional theory (DFT) were used by White et al. [11,12] to elucidate structural changes and molecular mechanisms of metakaolin based geopolymer. Rees et al. [13] monitored the kinetics of fly ash

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based geopolymer using in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic. Provis et al. [14,15] applied in situ energy-dispersive X-ray diffractometry (ED-XRD) to investigate the reaction kinetics of metakaolin based geopolymer. Schneider et al. [16] characterized the structure and composition of different alkali solution activated GGBS using ^{29}Si and ^{27}Al high-resolution NMR. Meanwhile, quantification of kinetics has not been possible in White's researches, and the presence of silica in activating solution hinders the application of ATR-FTIR spectroscopic technique. In addition, widespread use of these measurements is and will remain limited due to the restricted access to the equipment.

With the advantage of real-time information over other intermittently recording methods, isothermal calorimetric characterization has become a powerful technique in studying cement hydration kinetics [17–19]. Investigations of alkali-metakaolin and alkali-slag reaction systems have demonstrated that calorimetric measurement is powerful in obtaining the information needed for describing alkali activation [20–22]. However, the external mixing process in these studies failed to collect heat response during sample mixing and loading periods. Heat evolution of alkali activated metakaolin from the initial reaction has been recently measured and reported by Zhang et al. [23,24], but the interpretation of some features of the data sets is still open for discussion. In addition, much of the published work in this area focused on a single precursor per study, with limited scope for broader applicability of the results in selecting proper raw materials for different practical applications.

X-ray diffraction (XRD) is another prominent analytical technique in the characterization of cementitious system. While the calorimeter offers an insight into the time resolved heat evolution, in-situ XRD analysis provides the possibility of determining the dissolution and formation of mineral phases during reaction. Over recent years, the success of XRD has been rooted not only in detector performance, but also in the different quantification approaches, such as the Rietveld refinement and Partial Or No Known Crystal Structure (PONKCS) methods [25]. With the internal or external standards, Rietveld refinement has been used in quantifying mineral and the total amorphous phases. PONKCS, a blending of a profile summation method with the Rietveld method, facilitates the classification and quantification among different amorphous phases. Efforts have been made recently in determining the reaction degree of supplementary cementitious materials in blended cements [26–28]. In Williams's investigations [29,30], pilot works have been conducted in quantifying the mineral and amorphous phases of FA and MK based geopolymer, though measured either at elevated temperature (70 °C) or non-in situ. To date, progress in quantitative phase analysis of alkali activated slag and metakaolin has not been reported. Furthermore, investigations at ambient or a little higher temperatures are of more practical significance than that conducted at elevated temperatures in bolstering the in-field application of AAM.

In this study, the influence of the mix design on the reaction of NaOH activated FA, MK and GGBS will be first comparatively studied in terms of isothermal behaviours and mineralogy evolutions. Effects of alkali activator concentration, liquid-to-solid ratio, as well as curing temperature on the heat evolution were investigated using an isothermal calorimeter. Quantitative analysis of calorimetric data was undertaken by calculating the activation energy of each reaction system, which was further used to compare the temperature dependence of different precursors. In-situ XRD was adopted to measure the mineralogical development during reaction. Amorphous phases in source precursors and resultant products were distinguished and quantified, as well as the dissolution and formation of crystalline phases.

Table 1

Chemical composition of FA, MK and GGBS.

Parameter/compound	FA	MK	GGBS
	wt%	wt%	wt%
Loss on ignition	3.27	1.76	0.47 ^a
Al_2O_3	21.67	32.58	10.53
SiO_2	52.72	61.24	40.28
CaO	4.85	0.13	34.54
Fe_2O_3	9.55	1.17	0.39
MgO	1.89	0.15	8.63
P_2O_5	0.48	0.05	0.15
TiO_2	0.90	1.64	0.40
MnO	0.08	n. d.	1.14
Na_2O	1.11	0.17	0.59
K_2O	2.27	0.63	1.62
Na_2O -equivalent	2.61	0.58	1.66
Sulfur as SO_3	1.09	0.07	2.19
Sulfide	n. d.	n. d.	0.71
Chloride	0.009	0.010	n. d.
Carbon	2.30	0.03	0.02
Cr_2O_3	0.04	0.02	0.01
V_2O_5	0.05	0.03	0.01

^a Tested in protective gas atmosphere.

2. Materials and methods

2.1. Materials

The solid precursors FA, MK, and GGBS used in this study are commercially available materials. The bulk chemical compositions were determined using X-ray fluorescence and are shown in Table 1. The FA is a siliceous fly ash conforming to DIN EN 450–2. In terms of the main composition, the GGBS has a higher content of CaO but contains less Al_2O_3 than the FA and MK.

The particle size was measured and represented by the Blaine specific surface area value, which is 3253 cm^2/g for FA, 5397 cm^2/g for MK and 4224 cm^2/g for GGBS.

Mineral compositions of source precursors were measured by powder XRD and quantitatively analysed using Rietveld refinement and PONKCS methods (details about the measurement and quantification are given in Sections 2.4 and 2.5). The results are shown in Fig. 1 and Table 2. The terms “Amorphous” and “Amorphous-PONKCS” in Table 2 represent the results quantified using Rietveld refinement with internal standard and PONKCS method, respectively. Rutile was used as internal standard, which was primarily mixed with solid precursor for phase quantification. The broad humps centring at ca. 20–35° 2 θ for FA, 20–30° 2 θ for MK and 25–35° 2 θ for GGBS reflect the glassy structure. Quantification results indicate that the precursors are largely amorphous with small quantity of different mineral phases. In addition, it can be inferred from Fig. 1 and Table 2 that the PONKCS results agree well with the quantification using an internal standard.

Bulk composition has been used in most references for mix design of AAM. However, studies have shown that the amorphous phases are easily dissolved and participate in the reaction, while most crystals, such as mullite, quartz, magnetite, hematite, etc., remain relative inert during alkali activation [2,3,5]. Zhang et al. [31] demonstrated that using the chemical composition of amorphous phase to assess the reactivity of solid precursors is more appropriate than using the bulk composition. The chemical composition of amorphous phases was calculated by subtracting the mineral components from the bulk composition. The results are shown in Table 3.

The activator used was NaOH solution of three different concentrations (6 mol/L, 9 mol/L and 12 mol/L). NaOH solutions were prepared, cooled down to room temperature and stored for at least 24 h prior to use. Table 4 shows the oxide molar ratios of samples studied in this work, which were calculated based on the chemical compositions

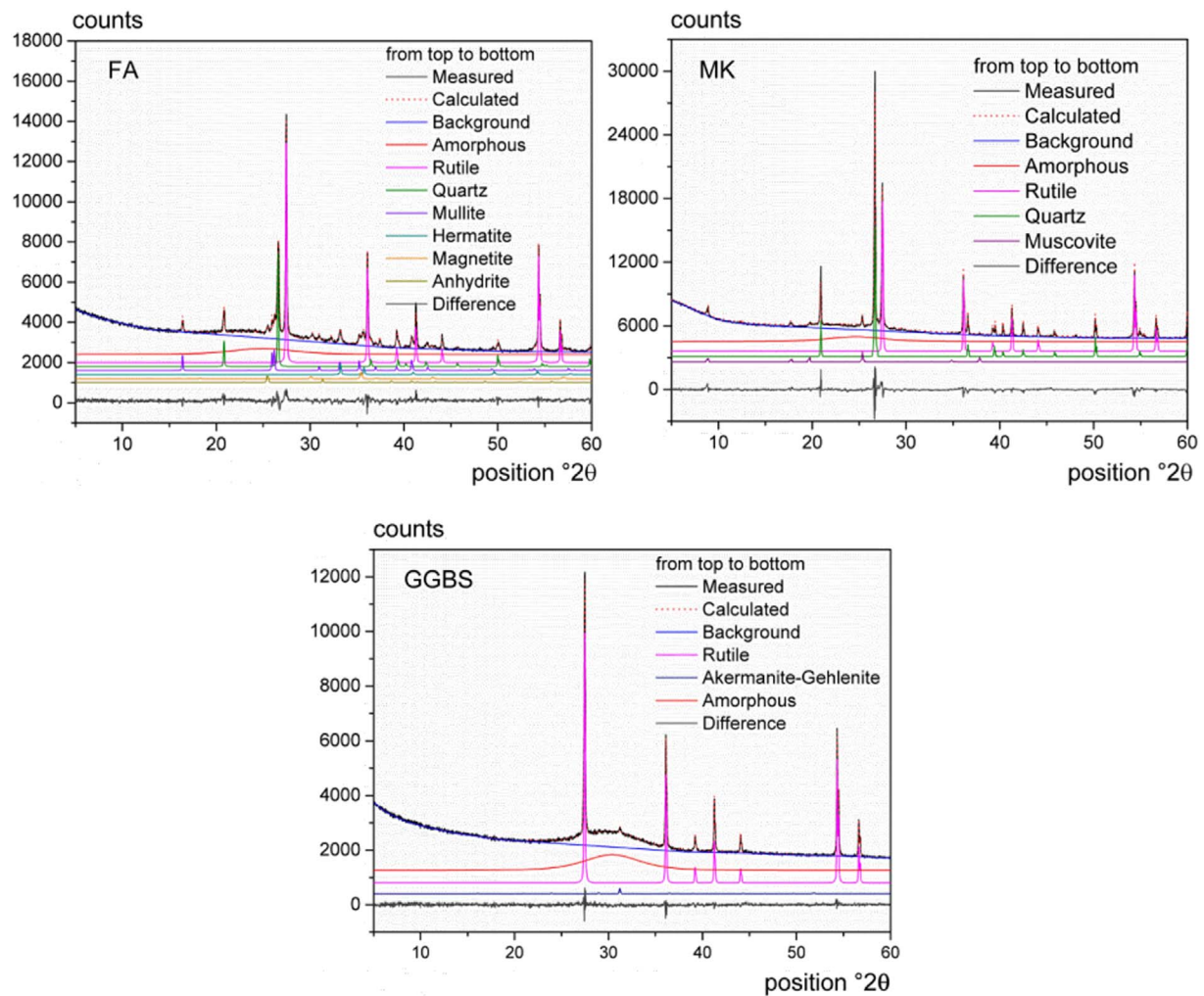


Fig. 1. XRD pattern and the PONKCS analysis results of FA, MK and GGBS.

Table 2
Mineralogical composition of FA, MK and GGBS.

Phase	PDF-Nr.	FA	MK	GGBS
		wt%	wt%	wt%
Mullite	98-008-0124	9.7	–	–
Quartz-low	98-005-6873	11.0	–	–
	98-002-3071	–	12.5	–
Magnetite	98-007-7842	2.2	–	–
Hematite	98-010-8081	2.5	–	–
Anhydrite	98-001-0223	1.4	–	–
Akermanite-Gehlenite	98-011-3072	–	–	5.1
Muscovite 3T	98-003-4922	–	3.3	–
Amorphous	–	73.0	84.1	94.9
Amorphous-PONKCS	–	72.9	84.1	94.8

of amorphous phases listed in Table 3. The letters in the sample ID represent the solid precursor used for sample synthesis, while the following numbers depict the associated solution concentration and the liquid-to-solid ratio, respectively. For example, FA-6-0.45 means that in this sample the fly ash was activated using 6 mol/L NaOH solution with a liquid-to-solid ratio of 0.45.

2.2. Isothermal calorimetry measurement

Heat evolution was measured using an 8 channel TAM Air isothermal calorimeter (TA Instruments, USA) equipped with admix

Table 3
Calculated chemical composition of the amorphous parts in FA, MK and GGBS.

Compound	FA	MK	GGBS
	wt%	wt%	wt%
Al ₂ O ₃	14.4	31.7	9.6
SiO ₂	39.1	47.1	38.5
CaO	4.2	0.1	32.4
Fe ₂ O ₃	4.7	1.0	0.4
MgO	1.9	0.1	8.2
TiO ₂	0.9	1.6	0.4
MnO	0.1	–	1.1
Na ₂ O	1.1	0.2	0.6
K ₂ O	2.3	0.3	1.6
Na ₂ O-equivalent	2.61	0.3	1.7
Others	4.3	2.2	2.0

ampoules for internal mixing. Preliminary tests were conducted to make sure that homogeneous pastes could be achieved for each reaction system even at the lowest liquid-to-solid ratio. Weighted solid precursor was loaded in a glass ampoule while the NaOH solution was held in plastic injector. The ampoule, injector and the mini-blender were set in the calorimeter until the thermal balance condition was reached. Heat evolution was recorded at the same time as the solution was injected into the ampoule and the mini-blender was started. Compared with the reaction heat, heat disturbance caused by the mini-blender could be neglected. The mixing procedure lasted 3 min and the calorimetric data

Table 4
Oxide molar ratios of NaOH activated FA, MK and GGBS.

Sample ID	SiO ₂ / Al ₂ O ₃	SiO ₂ / Na ₂ O	SiO ₂ / (Na ₂ O + CaO)	H ₂ O/ Na ₂ O	H ₂ O/ (Na ₂ O + CaO)
FA-6-0.45	4.6	4.3	2.8	13.1	8.8
FA-9-0.45	4.6	3.5	2.5	10.0	7.1
FA-12-0.45	4.6	3.2	2.3	8.8	6.4
FA-9-0.4	4.6	3.8	2.6	9.7	6.7
FA-9-0.5	4.6	3.2	2.4	10.2	7.4
FA-9-0.6	4.6	2.8	2.1	10.6	8.0
FA-9-0.7	4.6	2.5	1.9	10.9	8.5
MK-6-0.8	2.5	3.9	3.8	17.6	17.4
MK-9-0.8	2.5	3.0	3.0	12.6	12.5
MK-12-0.8	2.5	2.9	2.7	10.9	10.8
MK-9-0.7	2.5	3.4	3.4	12.6	12.5
MK-9-0.9	2.5	2.7	2.6	12.7	12.6
MK-9-1.0	2.5	2.4	2.4	12.8	12.6
GGBS-6-0.45	6.8	4.7	0.9	14.6	2.8
GGBS-9-0.45	6.8	3.8	0.9	10.9	2.5
GGBS-12-0.45	6.8	3.4	0.8	9.5	2.3
GGBS-9-0.4	6.8	4.1	0.9	10.7	2.3
GGBS-9-0.5	6.8	3.4	0.8	11.1	2.7
GGBS-9-0.6	6.8	2.9	0.8	11.3	3.1
GGBS-9-0.7	6.8	2.6	0.8	11.5	3.5

were recorded for a period at least 48 h.

2.3. Determination of activation energy

The Arrhenius equation (Eq. (1)) was applied to determine the activation energy (E_a) of NaOH activated FA, MK and GGBS. The exponential Arrhenius equation is based on collision theory, thus molecules are supposed to react if the latent energy of successful collision exceeds E_a [14,32].

$$\kappa t = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad (1)$$

- κ_t reaction rate constant at temperature T
- A proportionality constant
- E_a activation energy in kJ/mol
- R natural gas constant (8.314 J/mol/K),
- T absolute temperature in K

E_a can be obtained by plotting the natural log of reaction rate versus the inverse of the reaction temperature. According to Shi et al. [33] and Fernandez-Jimenez et al. [34], the Knudsen equation (Eq. (2)) is recommended to derive the global reaction rate constant κ_t either from the non-linear regression of the cumulative heat evolution curves, or from a linear regression of the plot between $1/Q_{(t)}$ versus $1/(t - t_0)$.

$$Q(t) = Q_{\infty} \cdot \frac{\kappa_t \cdot (t - t_0)}{1 + \kappa_t \cdot (t - t_0)} \quad (2)$$

- $Q_{(t)}$ cumulative heat release at time t in J/g
- Q_{∞} total heat release at $t = \infty$ in J/g
- t_0 end of the induction period

2.4. XRD measurement

The mineral phase developments during the first 24 h at 20 °C were in-situ measured using an X'Pert Pro Diffractometer (PANalytical, Netherlands) in the theta-theta geometry. CuK α X-rays were generated under 40 kV and 40 mA tube operating condition. As internal standard, 20 wt% of Rutile Kronos 2220 was thoroughly mixed with 80 wt% of FA, MK or GGBS. Reactants were manually mixed for 3 min, the homogeneous paste was then placed in a sample holder and covered

Table 5
Measurement settings for in-situ and powder XRD.

Parameter	Value	
	In-situ XRD	Powder XRD
Angular range	5–60° 2 θ	
Step	0.0167° 2 θ	
Measurement time	14:17 min	
Divergence slit	0.5°	0.125°
Incident anti-scatter slit	1.0°	0.25°
Receiving anti-scatter slit	5.5°	5.0°

with polyimide film to minimize carbonation and dehydration. The measurement settings are listed in Table 5. Under these data collection condition, 96 diffraction patterns were recorded during the total measurement time of 24 h.

The XRD measurement at 30 °C was conducted in semi in-situ way. The weighted solid and alkali activator solution were first heat treated at 30 °C in a laboratory oven. Sample preparation and XRD measurement were the same as that at 20 °C. After each measurement, the sample together with sample holder was transferred to an oven of 40 °C for 15 min prior to the next measurement. Since the measurements could only be performed at 20 °C, the sample cooled down during measurement and was warmed up in oven afterwards. Therefore the average temperature was around 30 °C. To minimize the effects caused by temperature fluctuation and time interval, three parallel measurements were carried out, each with 5 min interval. In other words, the first was measured immediately after the sample was prepared, while the second was first cured at 30 °C for 5 min and the third for 10 min before measurement. To assess the effects of temperature fluctuation on the semi in-situ XRD measurement at 30 °C, duplicate pastes were made and cured at 30 °C to specific time (1, 8, 12 and 24 h) for powder XRD measurements.

In addition, powder XRD measurements were also conducted on samples cured at 40 °C to further compare the effect of temperature on mineralogical development of NaOH activated FA, MK and GGBS. Following the RILEM TC-238 method [35], samples were crushed to meet the range of 125 μ m to 1 mm, 3 g of the powder was then mixed with 100 mL isopropanol for 15 min. The suspension was filtered and rinsed using isopropanol and diethyl ether, followed by the drying procedure at 40 °C for 8 min. Dried samples were then ground to pass through 63 μ m sieve for powder XRD measurements, which were conducted using a back loading sample holder and similar measurement settings as for the in-situ XRD measurements.

2.5. XRD data analysis

For the data analysis, XRD patterns of the reaction system were first achieved by subtracting the pattern of polyimide film. The film pattern was recorded following the method provided by Vollpracht [36]. Briefly, the film was mounted on a glass plate and measured for 5 times, using the same configuration as mentioned above. The same operation was conducted for the glass plate without film.

Rietveld refinement was carried out for quantitative phase analysis using the software HighScore Plus from PANalytical. PONKCS method was adopted to determine and quantify the amorphous in unreacted solid and reaction product. For Rietveld refinement, the {110} peak of Rutile was used as reference for the correction of specimen displacement caused by chemical shrinkage during in-situ XRD measurement. Refined parameters including cell and shape parameters were obtained by refining the raw materials. These parameters were kept constant and were not refined during analysis of the in-situ patterns. To derive the amorphous pattern of the raw materials using PONKCS method, a (hkl) phase was fitted to the precursor hump. The scale factor and profile parameters were refined, as well as the phase position by giving free

lattice parameter. The amorphous patterns corresponding to the reaction products of NaOH activated FA and MK were built in the similar procedure. The model for the amorphous phases generated in NaOH activated GGBS was modified on the basis of C-S-H pattern, which was developed following the method described by Bergold et al. [37]. To account for the pattern differences between the C-S-H and amorphous products in NaOH activated GGBS, the scale factor and profile parameters were uncoupled refined.

The dissolved ratio of amorphous phases after 24 h was computed as:

$$\alpha = \frac{f_{\text{initial}} - f_{\text{residual}}}{f_{\text{initial}}} \times 100\% \quad (3)$$

where, α represents the dissolved ratio, f_{initial} and f_{residual} are initial amorphous phase content in solid precursor (before reaction) and amount of amorphous phase in undissolved precursor after 24 h reaction, respectively.

3. Results and discussion

3.1. Effects of NaOH dosage on heat evolution

For a given solid precursor, the dosage of the alkali activator can significantly influence the reaction by changing the mix design of the system [2,5]. The activator dosage is generally adjusted by varying the solution concentration of specified liquid-to-solid ratio or vice versa. The effects of NaOH concentration on early stage heat evolution were studied at 20 °C and shown in Fig. 2.

An exothermic peak appears immediately when the activator is mixed with the solid material, which can be designated as the wetting and dissolution of solid material [33]. This narrow peak is similar to the initial (pre-induction) period of cement hydration process, although the potential physicochemical reactions may be significantly different [38]. The onset of the dissolution resulting in the first heat peak seems to be affected by the NaOH concentration, since the magnitude was enhanced by increasing solution concentration.

In contrast to Fig. 2c and e, Fig. 2a shows a single extensive exothermic heat response. No other remarkable heat features can be found even with increased activator concentration or prolonged reaction time. As widely accepted by many researchers, formation and polymerization of gels are responsible for the noticeable heat peaks following the dissolution period [38,39]. The heat flow in Fig. 2a after initial dissolution is weak but not zero, which can be clearly seen in the corresponding cumulative heat curves in Fig. 2b. The slow cumulative heat increase can be assigned to the continuous dissolution and slight transformation of dissolved species into gels, which accounts for over 98% of the reaction time measured but only 54% of the cumulative heat released. The low transformation degree might be responsible for the non-hardening of NaOH activated fly ash even after 24 h at 20 °C. Studies [3,40] also showed that negligible compressive strength was observed for alkali hydroxide activated fly ash cured at room temperature for days.

For the NaOH activated MK, the initial dissolution peak was followed by a short dormant period and another broad exothermic peak. After the initial dissolution process, the concentrations of dissolved ionic species reach a threshold for the outset of following reactions. The dormant period, which is entitled as induction period in cement hydration, is supposed to be the time needed for concentration growing up [33]. Both polymerization and condensation of geopolymeric gels are exothermic and make the main contribution to the second peak [38]. As shown in Fig. 2c and d, increasing the activator concentration broadens the heat evolution peak and increases the cumulative heat release.

The second exothermic peak can also be seen in the heat evolution curve of NaOH activated GGBS. The extensive precipitation of reaction products, such as C-A-S-H, is reported to be responsible for this broad peak [33,39]. An increase in activator concentration shortens the

induction period and contributes to the early arising of the second peak, which behaved differently from the NaOH activated MK.

The effects of solution concentration might be bilateral. On one hand, higher concentration involuntary accelerates the dissolution by providing more OH^- and consequently shortens the induction period [4,10], which is well reflected in Fig. 2e. On the other hand, reaction products precipitate fast on the surface of precursor grains [41]. This might be a barrier that affects the dissolution and diffusion of the ions into solution for gelation and polymerization [5,41], resulting in extended duration of this period and lowered magnitude. In Fig. 2d and f, in spite of the largest initial heat release of 12 mol/L NaOH activated MK and GGBS, in some period of the reaction the cumulative heat is lower than for 9 mol/L or even 6 mol/L NaOH, this might be caused by hindered dissolution. The actual influences of solution concentration are probably a concurrent result of both. With regard to the solution used in this study, higher concentration favours alkali activation when related to the cumulative heat release. It should be mentioned that the incremental of cumulative heat release when increasing activator concentration from 9 to 12 mol/L is nonsignificant, even extending the reaction time to 72 h. Thus, NaOH solution of 9 mol/L was adopted in the following sections. In addition, Palomo et al. [40] also reported that highly concentrated activator (> 18 mol/L) retards geopolymerization in terms of strength development. Therefore, preliminary tests are required for the decision of applicable activator concentration for a specific precursor.

Fig. 3 shows the effects of liquid-to-solid ratio on reaction heat of NaOH activated FA, MK and GGBS. Compared with the effects of NaOH concentration as shown above, the effects of liquid-to-solid ratio on reaction heat seems to be insignificant. From the results of Fig. 3, it can be inferred that there is an optimal liquid-to-solid ratio for alkali activation. A low liquid-to-solid ratio retards the reaction due to insufficient OH^- for the breakdown of covalent Si-O-Si and Al-O-Al bond in the glassy phases of solid precursor [5]. Higher liquid supply might facilitate the dissolution process. However, as shown in Table 4, the corresponding water content is also escalated while increasing the solution dosage of the same concentration, which might have negative effects on the following reactions of the dissolved species. This is reflected in the gradually delayed arise of the second exothermic peak summit in NaOH activated MK and GGBS, as well as decreased cumulative heat release shown in Fig. 3b, d and f, when continuously increasing the liquid-to-solid ratio surpassing the optimal one. Thus, the optimum liquid-to-solid ratio in this study would be 0.45 for FA and GGBS, 0.8 for MK. This liquid-to-solid ratio was adopted in Sections 3.2, 3.3 and 3.4, with the NaOH concentration of 9 mol/L.

3.2. Effects of temperature on heat evolution

Among the many processing factors, temperature plays a critical role in determining not only the setting but also the mechanical strength of AAM [5,9]. As depicted in Fig. 4, the influence of curing temperatures on heat evolution of NaOH activated FA, MK and GGBS was tested. The NaOH concentration used was 9 mol/L, and the liquid-to-solid ratio was of 0.45, 0.8, and 0.45 for FA, MK and GGBS, respectively.

Comparing with Figs. 2 and 3, curing temperature seems to have stronger and more complex influence on alkali activation than that of NaOH concentration and liquid-to-solid ratio. As aforementioned, the NaOH activated FA system exhibited a single-peak calorimetric response at 20 °C. However, the increase of curing temperature distinctly converts it into multiple-peak system. This is a clear indication of temperature dependence of NaOH activated FA. Chithiraputhiran et al. [39] reported that at room temperatures, polymerization or condensation in alkali hydroxide activated FA was minute due to the low reactivity and high activation energy barrier. It can be inferred from the multiple heat flow peaks that there are multiple chemical steps occurring. At elevated temperatures, exothermic structure transformations

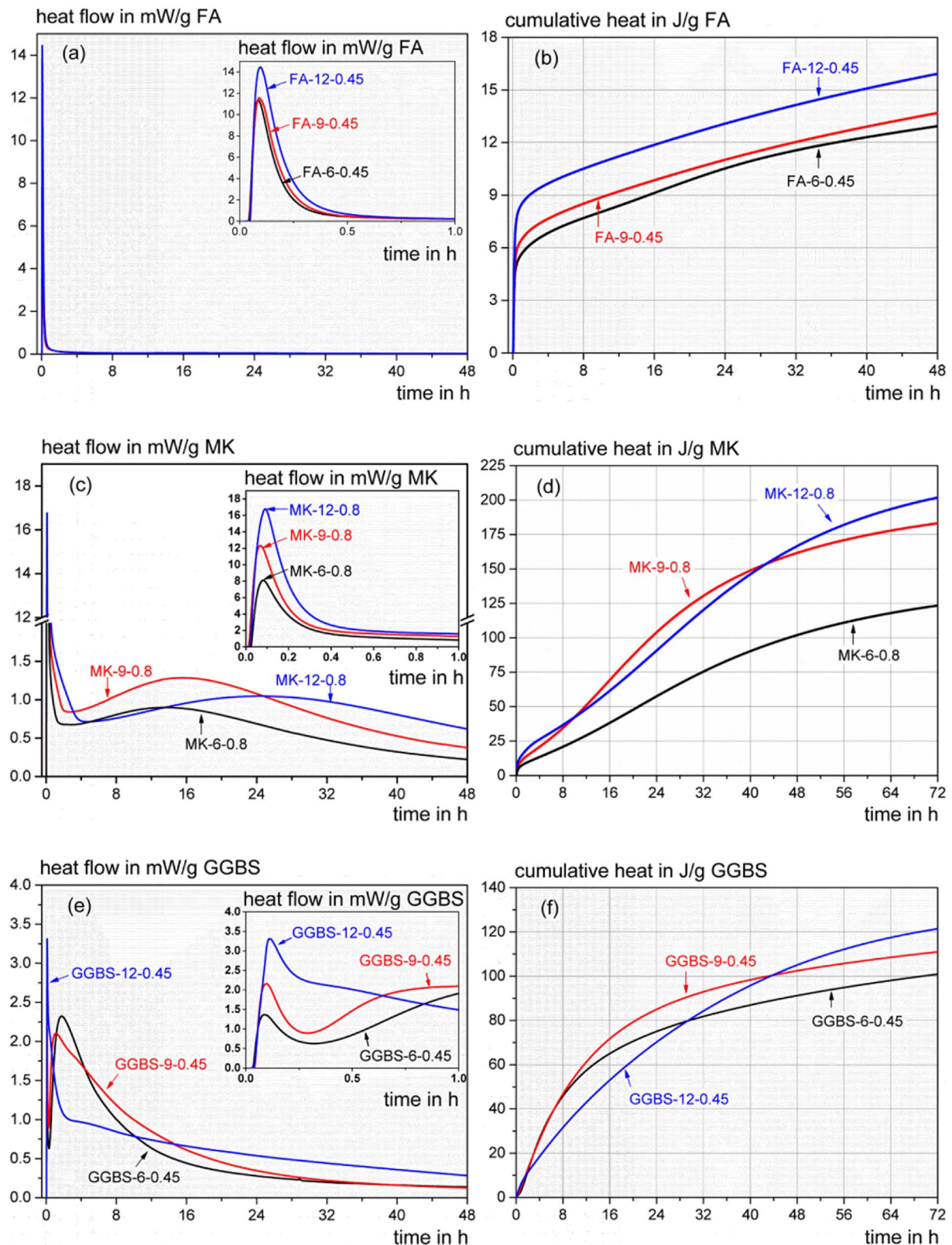


Fig. 2. Heat evolution of FA, MK and GGBS activated using NaOH of different concentrations.

develop, leading to the advent of new peaks. In Fig. 4a, an increase in temperature from 30 °C to 40 °C contributes to the further intensification and early emergence of these peaks. The 72 h cumulative heat release at 30 °C and 40 °C is 2.6 and 5.4 times of that at 20 °C, respectively.

As can be seen in Fig. 4c, though an increase in curing temperature did not bring forth the emergence of new peaks in NaOH activated MK, the shape and position of the second peak changed significantly. The peak magnitude of NaOH activated MK at 30 °C and 40 °C was about 3.4 and 10.8 times of its 20 °C counterpart, while the time needed to reach

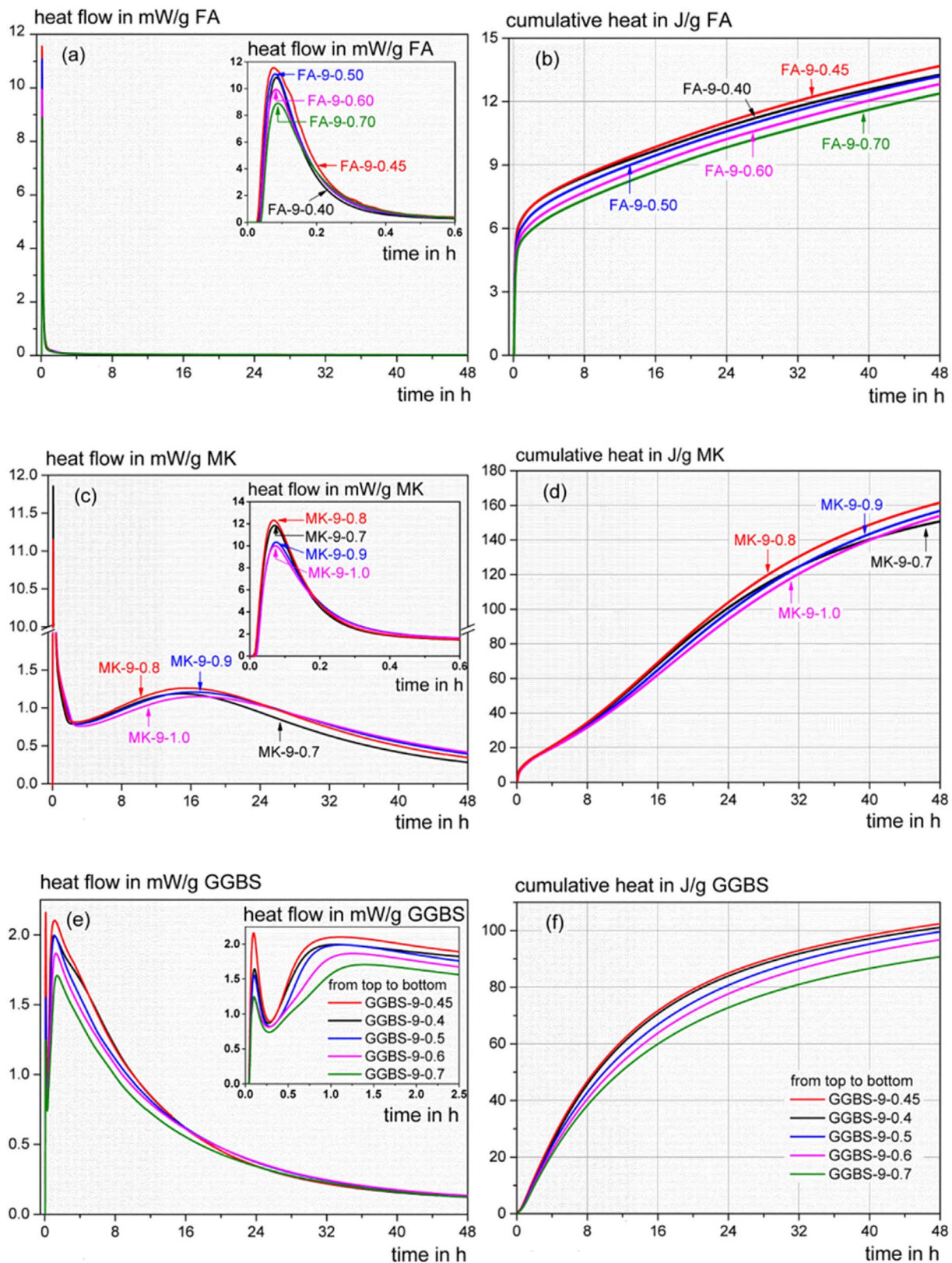


Fig. 3. Heat evolution of NaOH activated FA, MK and GGBS with different liquid-to-solid ratios.

summit of the second peak was shortened from 15.59 h to 4.29 h and 1.35 h after increasing the temperature from 20 °C to 30 °C and 40 °C, respectively. In addition, the increment of cumulative heat release of NaOH activated MK caused by temperature rise is much lower than NaOH activated FA, once again demonstrating the temperature

dependence of the latter.

Temperature increase also conducted to the position shift and amplitude enhancement of the second peak in NaOH activated GGBS. The early emergence of the second peak also resulted in the convolution with the initial one at higher temperatures. As displayed in Fig. 4e, a

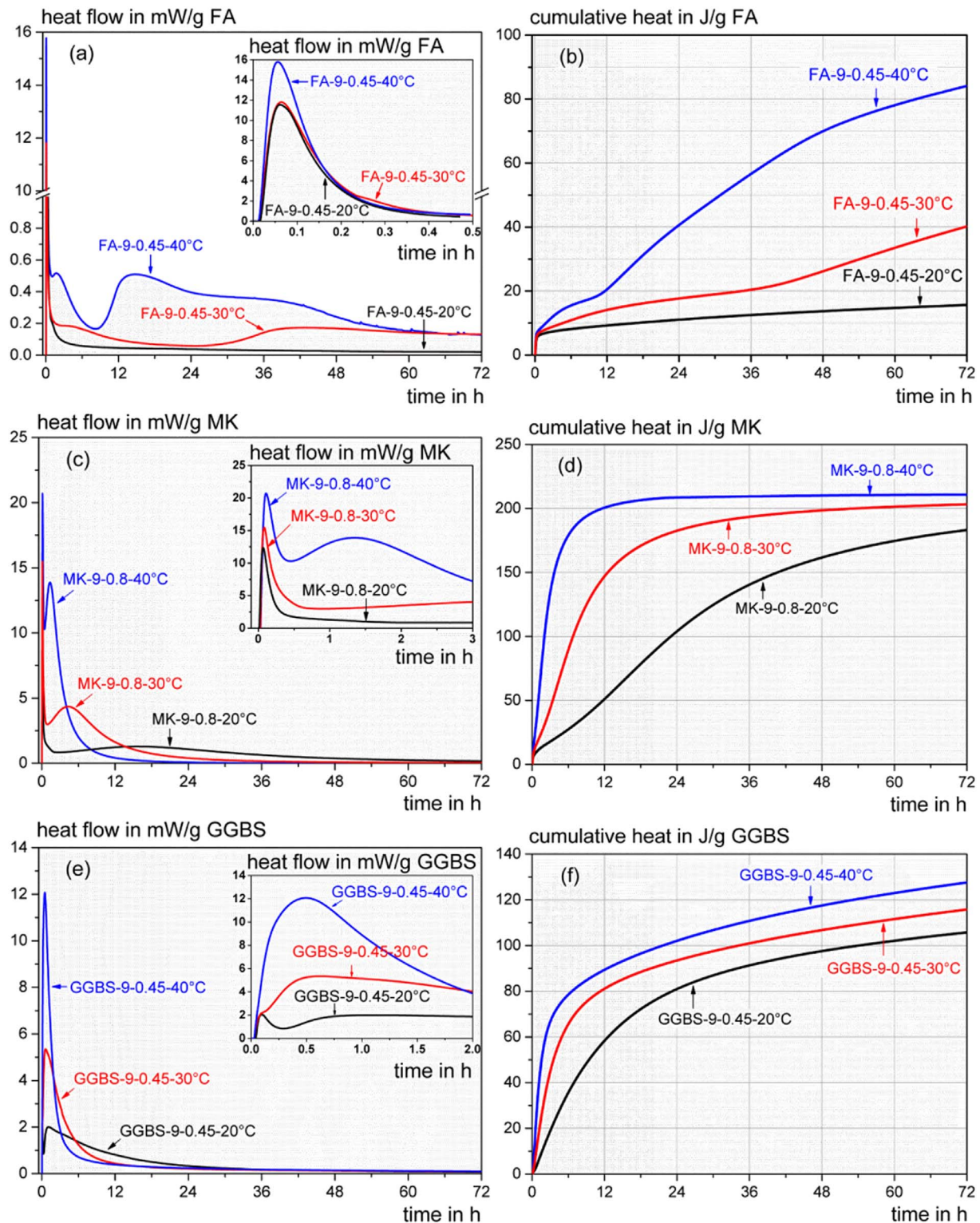


Fig. 4. Heat evolution of NaOH activated FA, MK and GGBS at different temperatures.

transition between both peaks can be observed at 30 °C which is less obvious at 40 °C, indicating an even accelerated reaction process.

The temperature dependence of chemical reactions is often formulated using the Arrhenius equation. Efforts have been well documented for cementitious system and alkali activated material [29,32,34,42]. Activation energies of NaOH activated FA, MK and GGBS were calculated as explained in Section 2.3 and are shown in Table 6, as well as compared to some results reported in literature

[32,34,43,44]. Considering the single peak property of NaOH activated FA at 20 °C, heat evolution at 60 °C was also documented (Supplementary Fig. S1) for the activation energy calculation of NaOH activated FA system. It is well known that caution must be paid when calculating and interpreting activation energy due to the highly lumped nature of reaction parameters [14]. In this study, the physical significance of E_a is limited to identify and compare the temperature dependence of solid precursors for alkali activation. As listed in Table 6,

Table 6
Activation energy of alkali activated FA, MK and GGBS.

E_a (kJ/mol)	Solid precursor	Liquid activator	Author and reference
86.2	Class F fly ash	8 mol/L NaOH	Skvára et al. [32]
60	70% GGBS + 30% OPC	Water	Barnett et al. [43]
34.6 ± 2.0	Metakaolin	4 mol/L NaOH	Gualtieri et al. [44]
57.6	GGBS	$\text{Na}_2\text{SiO}_3 + \text{NaOH}$	Fernandez-Jimenez et al. [34]
85.5 ± 4.6	FA		
46.3 ± 2.4	MK	9 mol/L NaOH	This work
48.2 ± 2.9	GGBS		

the activation energy of FA used corresponds to 85.5 ± 4.6 kJ/mol, which is of the same order as 86.2 kJ/mol obtained by Skvára et al. [32] using 8 mol/L NaOH activated FA. For alkali activated MK and GGBS, much lower activation energy than that of FA were reported in literatures [34,43,44], similar results were obtained in this work. According to Arrhenius, the activation energy E_a is the energy barrier that the solid source materials and alkali activator must overcome for further reaction, thus high temperature treatment of NaOH activated FA is necessary to promote geopolymerization.

3.3. Reaction products

Fig. 5 shows the mineral composition of NaOH activated FA and MK geopolymers at different temperatures.

For NaOH activated FA, most of the minerals from source material are unlikely to undergo chemical reactions during geopolymerization except anhydrite. The weakening and disappearing of diffraction peaks of anhydrite suggests the dissolution of this phase under high pH environment. New reflections at 14.02° , 24.34° and 34.42° 2θ can be attributed to the reflection of cancrinite ($\text{Na}_8(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{H}_{0.88}(\text{CO}_3)_{1.44})(\text{H}_2\text{O})_2$, PDF No. 98-001-8104). Cancrinite is a zeolite mineral belonging to the ABC-6 family, which is characterized by a basic structural layer consisting of six-membered rings of Al- and Si-tetrahedral [45]. Structural properties of cancrinite in alkali activated fly ash have been reported in [45], and the zeolite synthesis using fly ash has been well summarized by Querol [46]. Various studies [2,5,29] have stated the similarity of zeolite synthesis and geopolymerization, except that zeolite is usually synthesized under hydrothermal conditions around $150\text{--}200^\circ\text{C}$ in a diluted system. The role of zeolite phases in geopolymers is not clear yet, but most researchers affirm that the crystalline phases may not contribute much to the compressive strength of geopolymer [2,4]. The dissolution of anhydrite and the formation of

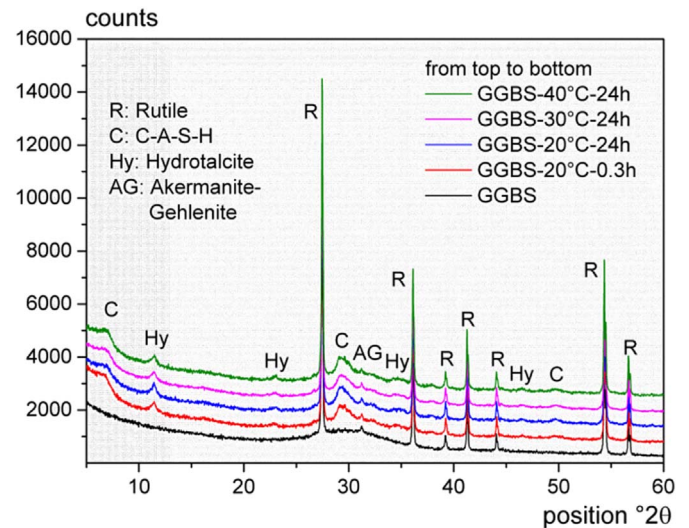


Fig. 6. XRD pattern of NaOH activated GGBS (NaOH concentration: 9 mol/L; liquid-to-solid ratio: 0.45).

cancrinite was detected in a short time (around 0.5 h), even at 20°C . The fast dissolution and formation of phases is further discussed in Section 3.4.

Due to the geopolymerization, a shift of the amorphous hump to higher 2θ angles can be identified in Fig. 5a, indicating the formation of a new amorphous phase [5]. Similar trends can also be found in NaOH activated MK, as shown in Fig. 5b. The new amorphous phase is a highly cross-linked, structurally disordered aluminosilicate gel, which is often represented as N-A-S-H [1,47].

In contrast, the NaOH activated GGBS forms predominantly C-A-S-H gel, which causes the reflections around 7° , 30° and 50° 2θ in Fig. 6. In addition, the octahedral aluminium not incorporated into the C-A-S-H forms other reaction products. Hydrotalcite ($((\text{Mg}_4\text{Al}_2)(\text{OH})_{12}(\text{CO}_3)(\text{H}_2\text{O})_{0.5})$, PDF No. 98-000-6182), for example, is one of these secondary products, with reflections at 11.6° , 23.3° , 34.9° and 46.8° 2θ in Fig. 6. Hydrotalcite possesses a brucite-type layer structure with the interlayer region containing CO_3^{2-} ions and water molecules [48].

3.4. Quantitative analysis of XRD results

Previously, the progress in quantitative XRD analysis of geopolymers and alkali activated slag was limited since both the unreacted solid precursors and reaction products contain amorphous or

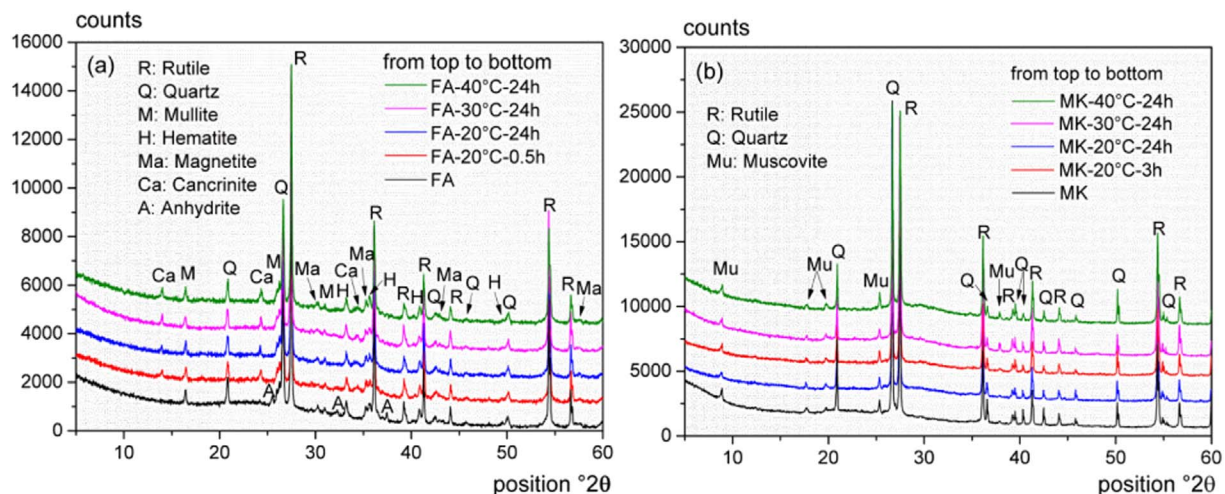


Fig. 5. XRD pattern of NaOH activated (a) FA, and (b) MK (NaOH concentration: 9 mol/L; liquid-to-solid ratio: 0.45 for FA, 0.8 for MK).

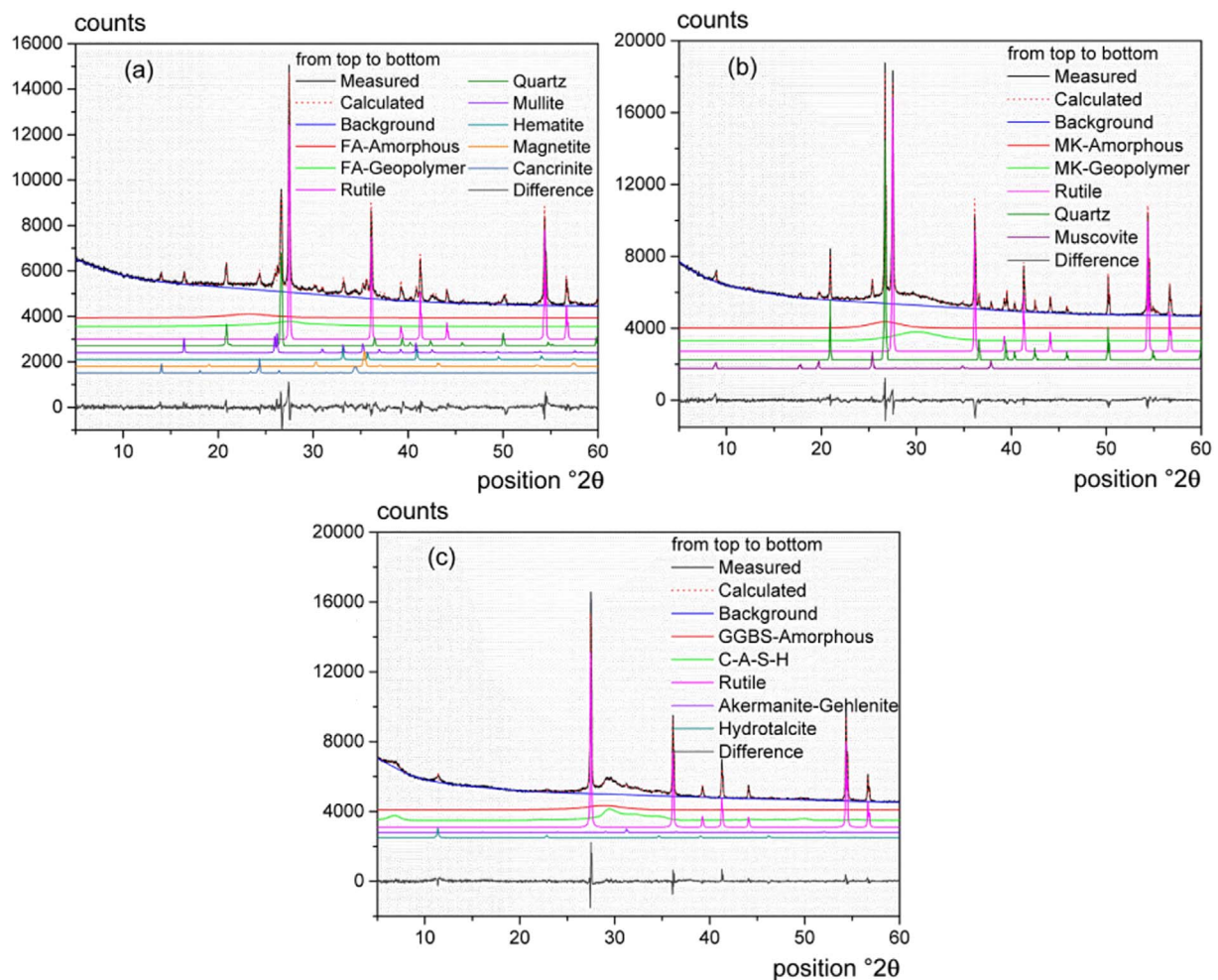


Fig. 7. Quantification of NaOH activated (a) FA, (b) GGBS and (c) MK by the POKKCS method.

nanocrystalline phases. The total amount of amorphous phases could be quantified using Rietveld refinement, but the exact proportions of residual unreacted source and newly formed gels could not be estimated [24]. Nowadays, with the development of XRD quantification approaches, progress has been made in fitting and quantifying amorphous phases of unreacted precursors and resultant products using the POKKCS method [25,27,30]. It should be noted that considerable time and efforts are prerequisites for good analytical practice for POKKCS method in obtaining reasonably accurate and meaningful results, especially for reaction systems containing GGBS, because of the high overlap of amorphous of source materials and reaction products [28]. The patterns of the amorphous reaction products were fitted and calculated as aforementioned. After introducing the calculated amorphous patterns of source materials, amorphous of unreacted source materials and the products could be distinguished and quantified. Profile parameters of the calculated amorphous patterns of source materials were kept constant except the scale factor during refinement. Fig. 7 gives a visual assessment of the application of the POKKCS method in quantifying the NaOH activated FA, MK and GGBS, and the quantification results are shown in Fig. 8. Samples are of the same composition as studied in Section 3.3.

As shown in Fig. 8, the amorphous of solid precursors expeditiously dissolved after contact with alkali activator. Dissolution rate decreased smoothly with time and equilibrated, which was comparable with the formation of amorphous geopolymer products. In Fig. 8a and b, formation of cancrinite launched coinstantaneous with the dissolution of mineral and amorphous phases in precursor. After 0.5 h of reaction, a plateau of cancrinite formation was reached in NaOH activated FA, and

the reflections which correspond to anhydrite have disappeared. The time 0.5 h roughly equals to the duration of the initial exothermal peak, which represents the dissolution stage of solid precursor.

The formation of hydrotalcite was also identified by the end of the first exothermic peak in NaOH activated GGBS. Williams et al. [29] illustrated that many crystallite seeds form during the precursor dissolution period and their concentration and crystallite size instantaneously increase to a plateau value.

The powder XRD conducted at 30 °C is compared with the in-situ results and shown in Fig. 8b, d and f. Results show that the semi in-situ measurement used in this work overestimates the reaction to some extent, especially at early periods. This might be caused by the acceleration of reaction rate during the oven curing at 40 °C.

Table 7 shows the dissolved ratios of amorphous phase calculated using Eq. (3). The dissolution rate and percentage are influenced by the reactivity of source material and temperature. Due to the low reactivity and high activation energy of FA, the formation of geopolymer gels is hindered at 20 °C, in which around 12.5% of the FA amorphous was dissolved within 24 h. An increase in temperature from 20 °C to 30 °C contributed significantly to the reaction by improving the dissolution extent by a factor of 2.0. In [29], dissolution extent of amorphous ranging from 29% to 54% was determined for sodium silicate activated fly ash at 70 °C. Apart from the enhancement of reaction extent, moderate improved curing temperature can also shorten the time needed to reach equilibrium. The reaction mechanism of NaOH activated fly ash is still limited in conceptual understanding. Systematic work is required, particularly with regard to unravelling the reaction kinetics and property tailoring of FA based geopolymer.

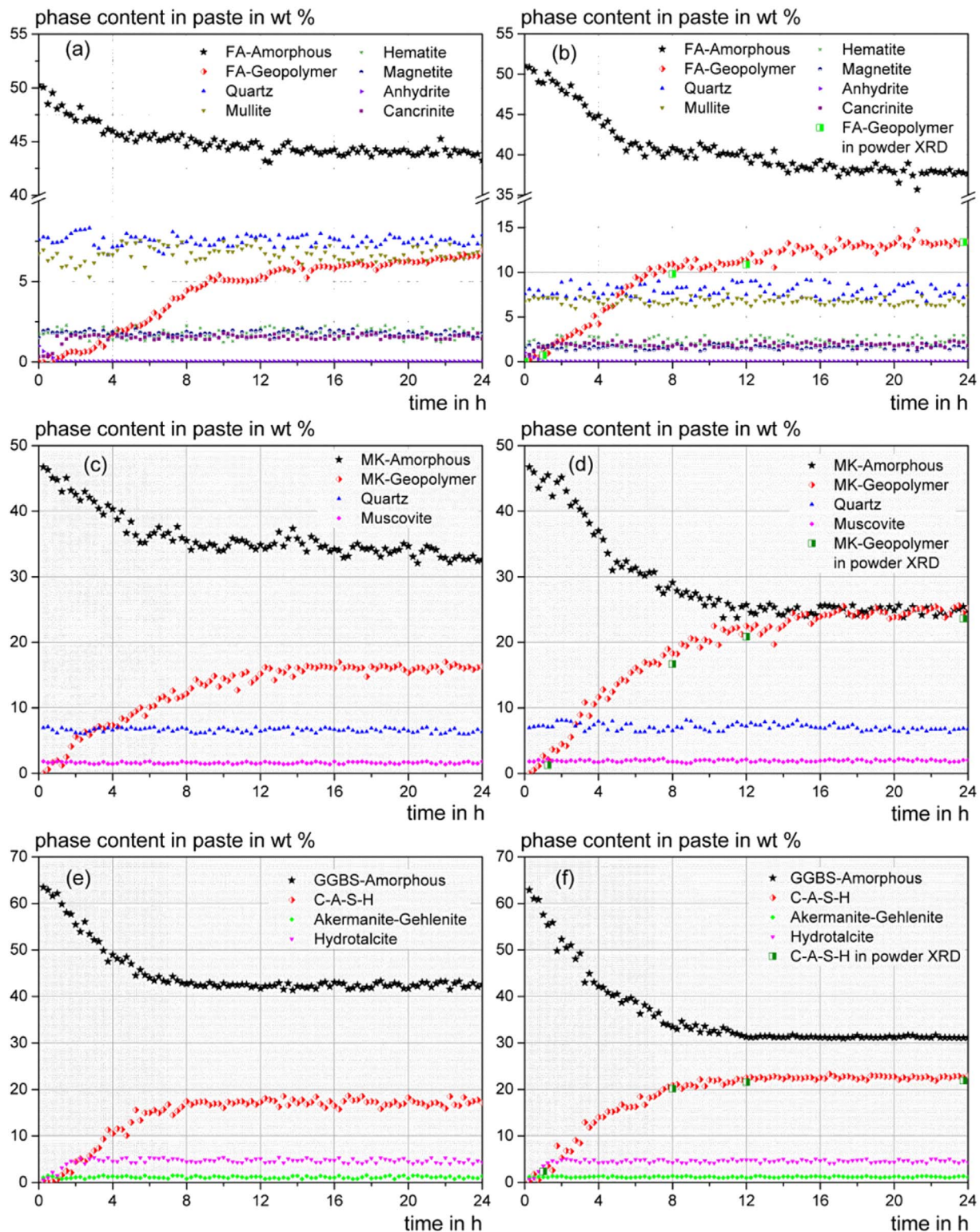


Fig. 8. Phase quantification of NaOH activated FA, GGBS and MK at 20 °C (left) and 30 °C (right) (NaOH concentration: 9 mol/L; liquid-to-solid ratio: 0.45 for FA and GGBS, 0.8 for MK).

Despite of the difference in reaction mechanism between NaOH activated MK geopolymer and NaOH activated GGBS, both MK and GGBS showed higher dissolved potential than that of FA because of the high reactivity. Raising the temperature further promotes the reaction of NaOH activated MK and GGBS. The improvement of amorphous dissolution was 46.6% for MK, and 52.4% for GGBS, when increasing temperature from 20 °C to 30 °C.

3.5. Correlation of calorimetry results with XRD measurements

Fig. 9 presents the correlation of products formation with heat release within the first 8 h. No secondary product has been detected in NaOH activated MK, thus the reaction product plotted in Fig. 9 is geopolymeric gels. For NaOH activated FA and GGBS, the reaction products include both the amorphous gels and crystalline phases generated during reaction. As aforementioned in this paper, the first

Table 7

Dissolution property of amorphous phase in FA, MK and GGBS.

Precursor	Amorphous content (wt%) ^a	Residual amount after 24 h of reaction (wt%) ^b		Dissolved proportion after 24 h of reaction (%) ^c	
		20 °C	30 °C	20 °C	30 °C
FA	72.9	63.8	54.6	12.5	25.2
MK	84.4	58.6	45.0	30.6	46.6
GGBS	94.8	61.2	45.2	35.5	52.4

^a Amorphous phase content in solid precursor before reaction (wt%).^b Amount of amorphous phase in undissolved precursor after 24 h reaction.^c Dissolved proportion of amorphous phase in precursor after 24 h reaction.

exothermic peak was mainly caused by the dissolution of solid precursors. During this time, amounts of heat have been released, but the valid detection of reaction products was no earlier than the end of the first peak. All these were reflected as the intercept in Fig. 9. The differences between the slopes of the best fit lines at different temperature might be caused by several reasons, for example, the structural diversities of gels. Though the main reaction products are X-ray amorphous, the ordering and coordination of Si and Al vary with temperature [38]. Details about such differences deserve further investigation.

Nevertheless, results show that the formation of reaction products correlates well with the heat evolution, demonstrating that the combination of isothermal calorimeter and in-situ XRD can enrich the quantitative analysis toolkit of alkali activation.

It can be concluded from Fig. 4 that the reaction is still ongoing after 8 h since the cumulative heat increases significantly. However, dissolution of source materials and formation of reaction products gradually reaches an equilibrium (Fig. 8). The cumulative heat gain might be caused by the further condensation and reorganization of N-A-S-H and C-A-S-H gels, but these transformations are not notable for XRD measurement [1,24].

The authors are highly aware that though the quantitative analysis based on POKCS methods promotes a better understanding of the mechanism of alkali activation, much work is still required to cross-check the POKCS method with other characterization techniques, such as mechanical strength testing, FTIR, NMR, etc., in optimising the analysis protocols.

4. Summary and conclusion

In this work, isothermal calorimeter and in-situ XRD were used to study the heat and mineral evolution of NaOH activated FA, MK and GGBS. Following conclusions can be drawn according to this study:

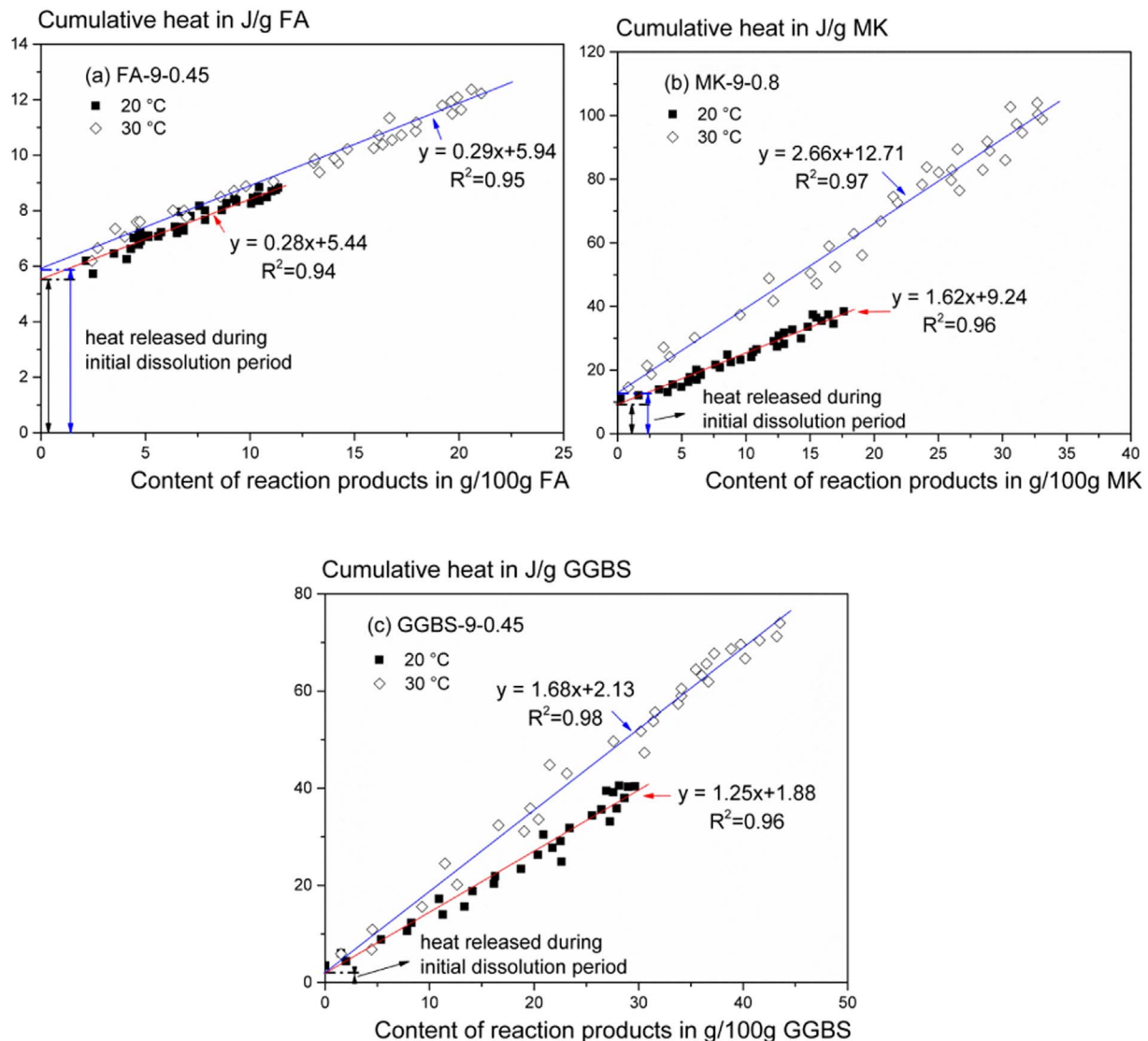


Fig. 9. Correlation of the first 8 h cumulative heat release with reaction products at 20 °C and 30 °C.

- (1) At 20 °C, NaOH activated FA showed single exothermic heat response, while in NaOH activated MK and GGBS, the initial dissolution peak was followed by a short dormant period and another broad exothermic peak. An increase in activator concentration extends the duration of the second peak.
- (2) The reaction of NaOH activated FA is more temperature dependent: raising temperature from 20 °C to 30 °C and 40 °C converts the single-peak calorimetric response into multiple-peak system, and enhances the 72 h cumulative heat release by 2.6 and 5.4 times, respectively. In comparison to NaOH activated MK and GGBS, the activation energy of NaOH activated FA is much higher.
- (3) NaOH activated FA and MK consist predominantly geopolymeric gels of N-A-S-H, while NaOH activated GGBS is mainly composed of C-A-S-H. Secondary products have been found in NaOH activated FA and GGBS, which are cancrinite and hydrotalcite, respectively. Formation of the crystalline phases is rapid and takes place during the initial dissolution phase indicated by the first calorimetric peak.
- (4) The dissolved rate and percentage of the amorphous are influenced by the reactivity of source material and temperature. Both MK and GGBS exhibit higher dissolution ratios than FA, while a slight increase of temperature from 20 °C to 30 °C doubles the dissolution ratio of NaOH activated FA.
- (5) The in-situ XRD measurements coupled with POKCS method used in this study are capable in quantifying the very early age formation of N-A-S-H and C-A-S-H gels. But further cross-checking work is still required to optimise the analysis protocols. In addition, other state-of-the-art techniques are needed, especially for better understanding of the medium- or long-term geopolymerization.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cemconres.2017.10.004>.

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Supplementary data:

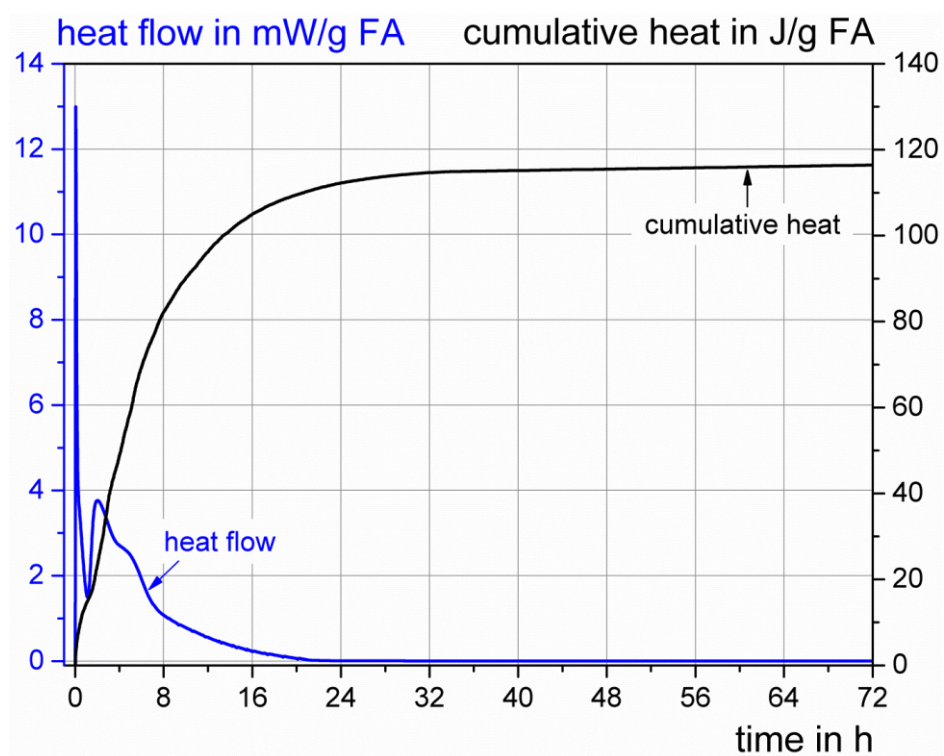


Fig. S1 Heat evolution of 9 mol/L NaOH activated FA at 60 °C

(liquid-to-solid ratio: 0.45)



One year geopolymerisation of sodium silicate activated fly ash and metakaolin geopolymers

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ABSTRACT

This paper presents the evolution of mechanical and chemical properties of sodium silicate activated fly ash and metakaolin geopolymers in one year time scale. The initial curing protocols are considered, which were chosen based on the isothermal heat release properties of both reaction systems. Increasing initial temperature contributes to the cumulative heat release, strength development and zeolite formation of both geopolymers, especially the fly ash based, but results in slightly worse pore characteristics. The formation of zeolite is rapid, indicating a simultaneous process with geopolymerisation. During sample handling and aging, natural carbonation took place. Two kinds of carbonation processes are detected: reaction of CO₂ with mobile alkalis on the one hand and with framework oxygen atoms of the aluminosilicate gels on the other hand.

1. Introduction

Geopolymer, a terminology first coined by Joseph Davidovits in the 1970s, refers to a class of materials synthesized via the reaction of solid aluminosilicates with an alkaline solution [1]. The geopolymer technology is in many instances regarded as a subset of alkali activated materials (AAMs) [2]. The most frequently used solid precursors for geopolymer synthesis are low calcium fly ash (FA) and metakaolin (MK), alkali metal hydroxide and silicate are the prevalent activators [2]. The contact of solid precursors and activator induces the dissolution of reactive component of the former, the released aluminates and silicates then undergo a multistep process, such as reorientation, gelation, and condensation, to form hardened geopolymeric materials [2–4]. Advanced investigations have revealed that the primary reaction product of geopolymer is an alkali aluminosilicate-type gel (N-A-S-H), which is also the key strength-giving component [2,3]. Both silicon and aluminium are of tetrahedral coordination in N-A-S-H [2,5]. Substitution of silicon by aluminium is detected within the gel framework, with the associated negative charge being balanced by alkali cations [5]. Studies also reveal that the N-A-S-H gel shares the nanostructural features of zeolites in chemical sense, but lacks long-range crystalline order [2,6,7].

Geopolymers possess superior engineering properties, which include but are not limited to high early and final strength, thermal and fire resistance, stability under chemical attack, strong adhesion to metallic and non-metallic surfaces, etc [1–3,6]. As performance-based

specifications become more prevalent, geopolymer based materials are now attracting attention from both academic and industrial fields. Parameters affecting the reaction kinetic and strength development have been extensively studied [4,8]. Findings from these groundbreaking researches deepened the understanding of geopolymerisation. However, most of these studies focus on a short time scale. Since the structural concretes are designed to last for several decades, medium- and long-term studies are essential and helpful in understanding the service life of geopolymers.

In 2006, Wallah and Rangan [9] conducted extensive work on characterizing the development of compressive strength, creep and drying shrinkage of fly ash based geopolymer concrete. A lack of mechanism study curtailed the value of this pioneering work. The effects of mix design on phase stability of geopolymer were investigated by De Silva and Sagoe-Crenstil [10]. In Lloyd's work, the macro and micro properties of geopolymers were characterized [11]. Both researches promote the understanding of geopolymer, but the 7 months heat treatment used in Ref. [10] is unsuitable for engineering applications and the accelerated aging method from Ref. [11] is open for discussion. Recently, Ye et al. [12] reported the properties of aged geopolymer synthesized using the mixture of bauxite tailing and ground granulated blast furnace slag (GGBS). But the special mixture shortens the significance of the findings. Studies in terms of mechanism and mechanical properties of typical geopolymers are more fundamental to deepen the understanding of the reaction mechanisms and promoting the application of geopolymers.

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In addition, this kind of work can fulfil the knowledge gap between geopolymerisation and durability of geopolymer. The limited record of durability is one of the limitations hindering the commercial adoption of this material at present. Durability is regarded as the interactions between material and the environment, which is strongly dependent on the physicochemistry of material [13]. Though more findings have been achieved in durability of alkali activated slag [13–15], relevant conclusions cannot be used for geopolymers because of the differences in chemistry. For example, higher direct chloride binding degree has been detected in geopolymers than in Ca-rich systems [16,17], which is partially assigned to the more porous property of N-A-S-H gel than C-A-S-H [13]. Meanwhile, more serious chemical disruption was reported in C-A-S-H based binders than in geopolymers after being exposed to high CO₂ atmosphere [18]. Reasons for this are still unclear, revealing the structural and chemical properties of gel is supposed to be helpful in exploring the mechanism. It should be pointed out that the well accepted chemical and structural information of N-A-S-H gel are based on early age reaction results. Long-term characterisation is required, since extended aging and continuous geopolymerisation might influence the chemistry and structure of the gels.

It therefore becomes essential to understand both the engineering properties and gel chemistry in an extended time scale. In this work, the evolution of strength, porosity and reaction products of sodium silicate activated fly ash and metakaolin geopolymers were studied in one year scale. The effects of the initial curing procedure were taken into consideration and correlated to the early age heat release properties. The reaction products were characterized using powder X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). Findings of this work are fundamental and preliminary for further quantitative studies.

2. Materials and methods

2.1. Materials

The FA and MK used in this study are commercially available materials, which are the same as used in Ref. [19]. Table 1 depicts the bulk compositions of both solid precursors determined using X-ray fluorescence (XRF). Powder XRD was applied to document the mineral composition of both precursors, the obtained data (details about the measurement and data analysis are given in section 2.5) are shown in Fig. 1 and Table 2.

Given that the amorphous phases are easily dissolved during

Table 1
Chemical composition of FA and MK.

Parameter/Compound	FA	MK
	wt. %	wt. %
Loss on ignition	3.27	1.76
Al ₂ O ₃	21.67	32.58
SiO ₂	52.72	61.24
CaO	4.85	0.13
Fe ₂ O ₃	9.55	1.17
MgO	1.89	0.15
P ₂ O ₅	0.48	0.05
TiO ₂	0.90	1.64
MnO	0.08	–
Na ₂ O	1.11	0.17
K ₂ O	2.27	0.63
Na ₂ O-equivalent	2.61	0.58
Sulfur as SO ₃	1.09	0.07
Chloride	0.009	0.010
Carbon	2.30	0.03
Cr ₂ O ₃	0.04	0.02
V ₂ O ₅	0.05	0.03

–: not determined.

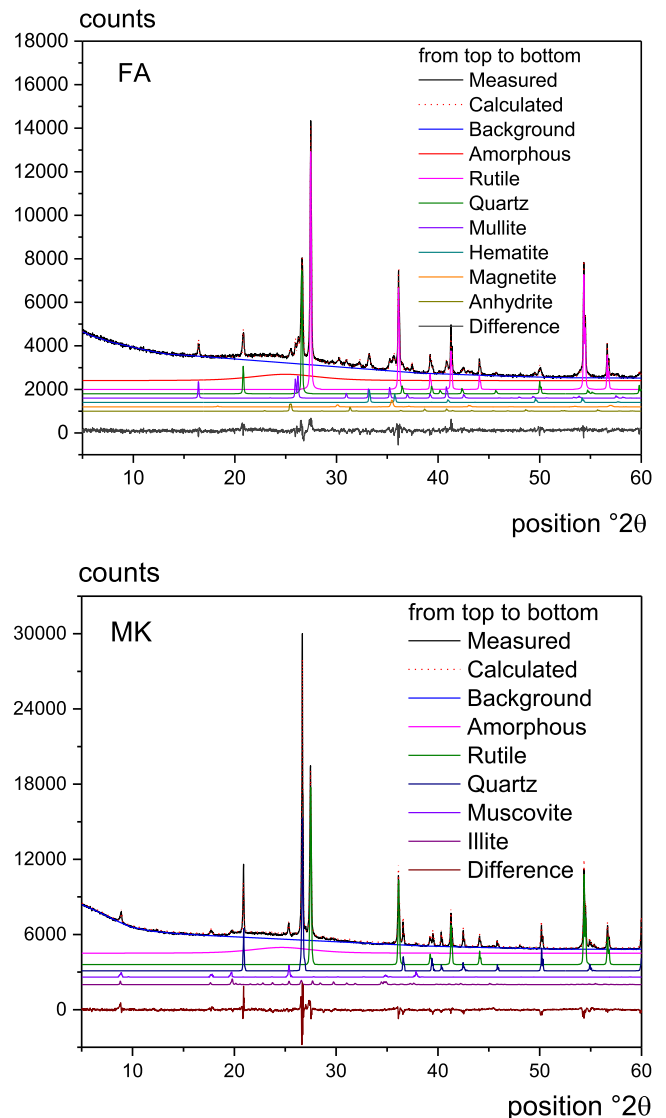


Fig. 1. XRD results of FA and MK [19], (Rutile was added as internal standard).

Table 2
Mineralogical composition of FA and MK.

Phase	PDF-Nr.	FA	MK
		wt. %	wt. %
Mullite	98-008-0124	9.7	–
Quartz-low	98-005-6873	11.0	–
	98-002-3071	–	12.5
Magnetite	98-007-7842	2.2	–
Hematite	98-010-8081	2.5	–
Anhydrite	98-001-0223	1.4	–
Muscovite 3T	98-003-4922	–	3.3
Illite	98-005-6872	–	1.8
Amorphous	–	73.0	82.4

geopolymerisation leaving most of the crystalline phases in FA and MK remain more or less inert, the chemical compositions of the amorphous phases were calculated following the method provided by Zhang et al. [20]. The results are shown in Table 3.

The activator used was sodium silicate solution, which contains 23.7 wt % SiO₂, 16.4 wt % Na₂O and 59.9 wt % H₂O. The modulus (SiO₂/Na₂O molar ratio) of the activator is 1.5. Composition of main components of the geopolymer synthesized in this work was calculated

Table 3
Calculated chemical composition of the amorphous parts in FA and MK [19].

Compound	FA	MK
	wt. %	wt. %
Al ₂ O ₃	14.4	30.2
SiO ₂	39.1	46.7
CaO	4.2	0.1
Fe ₂ O ₃	4.7	1.0
MgO	1.9	0.1
TiO ₂	0.9	1.6
MnO	0.1	–
Na ₂ O	1.1	0.2
K ₂ O	2.3	0.2
Na ₂ O-equivalent	2.6	0.3
Others	4.3	2.3

and listed in Table 4. The calculation was based on the chemical composition of amorphous phases in Table 3 and the mixing proportion.

2.2. Isothermal calorimetry measurement

The effects of temperature on the heat evolution of sodium silicate activated FA and MK geopolymers were measured using an 8 channel TAM Air isothermal calorimeter (TA Instruments, USA). The calorimeter is equipped with admix ampoules for internal mixing, which facilitates recording the heat response from the initial period. Solid precursor and activator were weighted and stored in glass ampoule and plastic injector, respectively. The ampoule, injector and the mini-blender were assembled together and set in the calorimeter. After the thermal balance condition was reached again, the measurement was started simultaneously when activator was injected into the ampoule and the mini-blender was switched on. The mixing procedure lasted 3 min and the calorimetric data were continuously documented for 72 h.

2.3. Sample preparation and strength measurement

Geopolymer mortars were produced by mixing weighted source materials in a planet mixer. The ratio of liquid activator-to-solid precursor (liquid-to-solid ratio) was 0.45 for FA and 0.75 for MK. These values were determined based on pre-test to ensure acceptable workability of the fresh geopolymer mortars and excellent mechanical properties after setting and hardening. For both FA and MK geopolymers, the mass ratio of sand-to-binder $s/b = 3$ is kept constant. CEN standard sand according to European standard EN 196–1 was used. All the solid precursors, liquid activator and sand were stored at 20 °C.

After 5 min mixing at 20 °C, fresh mortar was casted into moulds of $40 \times 40 \times 160 \text{ mm}^3$ and vibrated for 2 min to remove entrained air bubbles. Samples together with the moulds were then subjected into different curing conditions, i.e. 20 °C, 30 °C-12 h, 30 °C-24 h, 40 °C-12 h, 40 °C-24 h, 60 °C-12 h, 60 °C-24 h. The 12 h and 24 h represent the duration of initial heat treatment. The 20 °C cured samples were covered with a glass plate over the moulds and directly transferred into curing box of 20 °C and approx. 100% relative humidity (RH) for 24 h. Those samples cured at elevated temperatures were sealed in plastic bags and then stored in an oven with the specific temperature. The procedure of sealing in a plastic bag is based on the results of [21,22] and our pre-tests. Criado et al. [21] reported that this condition is better

than dry and steam curing for the strength development of geopolymers. The sample ID is titled as 'solid precursor - initial curing condition - age'. For instance, FA-20 °C-28 d represent 28 d aged FA geopolymer mortars initially cured at 20 °C (100% RH) for 24 h and MK-30 °C-12 h-28 d represents MK samples firstly cured at 30 °C for 12 h (sealed). After the designed curing at the corresponding temperature, samples were demoulded, wrapped by PE-foil and further stored at 20 °C and 65% RH until the strength measurement.

At an age of 3, 7, 14, 28, 96, 180 and 365 days, flexural and compressive strength were measured following DIN EN 196–1. The flexural strength was tested using the three point loading method. The distance between the supports was 100 mm and the load was applied at mid span with a rate of 0.05 kN/s. Three mortars of each group were used for the flexural strength test, and the resulting six halves were used for compressive strength measurement, with the force rate of 2.4 kN/s.

2.4. Porosity measurement

Porosity evolution and pore radius of mortar samples cured at 20 °C and 60 °C-12 h was measured using mercury intrusion porosimetry (MIP). Cubic samples of $40 \times 40 \times 40 \text{ mm}^3$ were produced and cured under the same conditions as described above. At the age of 7, 28, 180 and 365 days, the inner part (at least 5 mm from the surface) was crushed into small pieces. The crushed samples were oven-dried at 60 °C to remove the physically absorptive water in capillary pores. Around 10 g dried specimen was placed into the glass penetrometer for MIP tests. Both low and high pressure measurements were performed with the pressure ranging from 2 to 61000 psi. The intrusion and evacuation of mercury were automatically controlled by computer with Autopore IV 9500 program (Micromeritics Instrument Corporation, USA).

2.5. XRD measurement and data analysis

The mineral composition of solid precursors and geopolymers were measured using an X'Pert Pro Diffractometer (PANalytical, Netherlands). To quantify the mineral composition in solid precursors, Rutile Kronos 2220 was used as internal standard. 20 wt % of Rutile was thoroughly mixed with 80 wt % of FA or MK before measurement. For the measurement of geopolymer, pastes were prepared and cured under the same conditions as the corresponding mortar samples described in section 2.3. At specific testing times, reaction was stopped prior to sample preparation following the RILEM TC-238 method [23]. In brief, pastes were crushed to pass through 1 mm sieve, 3 g of the crushed specimen was then immersed in 100 ml isopropanol for 15 min. The suspension was filtered and rinsed using isopropanol and diethyl ether. Obtained samples were dried at 40 °C and ground to fine powders under $63 \mu\text{m}$. The measurement was conducted in the theta-theta geometry over the 2θ range of 5–60°, and CuK α X-rays were generated under 40 kV and 40 mA tube operating condition. The obtained data were analysed using the software HighScore Plus from PANalytical. Details about the data analysis procedure can be found in Refs. [19,24].

2.6. FTIR measurement and data analysis

FTIR was applied to characterize the gel chemistry of geopolymers synthesized in this work, which was conducted using NEXUS 670 (Nicolet, USA) spectrometer in absorbance mode. Pastes were produced

Table 4
Molar ratios of the geopolymer systems.

Sample	SiO ₂ /Al ₂ O ₃	SiO ₂ /Na ₂ O	SiO ₂ /(Na ₂ O + CaO)	H ₂ O/Na ₂ O	H ₂ O/(Na ₂ O + CaO)
FA geopolymer	5.86	5.14	3.51	9.30	6.35
MK geopolymer	3.62	5.28	5.23	12.27	12.17

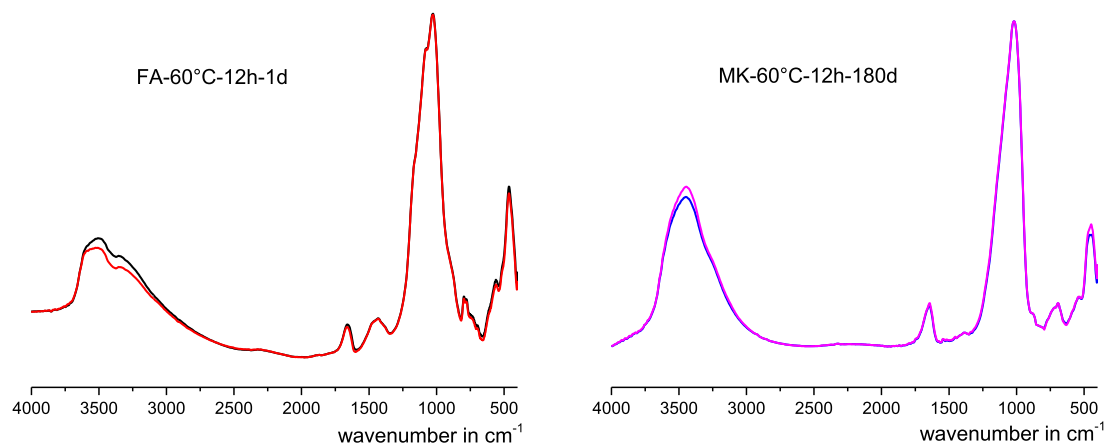


Fig. 2. Repeatability of the FTIR measurement.

and pre-treated in the same protocol as described in XRD measurement. The KBr pellet method was used to prepare the samples. All FTIR absorption spectra were documented in the range of $4000\text{--}400\text{ cm}^{-1}$ with a sensitivity of 2 cm^{-1} . Given the complexity of the sample preparation for solid FTIR measurement, samples were mixed with KBr and measured more than once to confirm that a good repeatability was achieved throughout the measurement. As shown in Fig. 2, no noticeable wavenumber shifts can be seen within the repeated measurements. The small differences at 3500 cm^{-1} might be due to small temperature and humidity variations.

3. Results and discussion

3.1. Effects of temperature on heat evolution

Among many processing factors, temperature plays a significant role in determining the setting, hardening and strength development of resultant geopolymers. Fig. 3 shows the influence of initial reaction temperature on heat evolution of sodium silicate activated FA and MK geopolymers. For both geopolymers produced at different temperatures, an exothermic peak arises immediately after mixing the activator with solid precursors. This narrow peak can be assigned to the wetting and dissolution of solid materials [25]. The onset of this peak is significantly affected by the initial reaction temperature, since the peak magnitude is enhanced by increasing temperature.

For the FA system, the normalized heat release gradually decreases after the initial exothermic peak. The afterwards heat flow of FA geopolymer at 20°C is weak but not zero, as shown by the slight increase of the corresponding cumulative heat curve in Fig. 3(b). The slow heat evolution is designated as the continuous dissolution of the solids and slight formation of geopolymeric gels [25,26]. Meanwhile, no other remarkable exothermic heat peak can be found even at elevated temperatures. This is different from our previous study in terms of NaOH activated FA, in which increasing temperature from 20°C to 30°C and 40°C distinctly converts the single-peak calorimetric response at 20°C into multiple-peak system [19]. The lower alkalinity of the sodium silicate used in this work probably causes these differences.

It can be seen from Fig. 3(b) that increasing temperature significantly enhances the cumulative heat release. The 72 h heat release of samples at 60°C , 40°C and 30°C is 11.7, 5.2 and 3.6 times of their 20°C counterpart, respectively. In addition, the heat release is more intense at elevated temperatures. The cumulative heat of FA geopolymer at 40°C seems to increase after 72 h, while the one at 60°C gradually equilibrates after 24 h.

For the MK geopolymer system, a broad exothermic peak can be found following the dissolution peak (Fig. 3(c)). At 20°C the second

peak is much lower than at the elevated temperatures, but can still be inferred from the close to linear cumulative heat increase till 36 h in Fig. 3(d). The condensation process of geopolymeric gels is exothermic. The emergence of the second peak demonstrates the extensive geopolymerisation in MK geopolymer. Increasing temperature significantly changes the shape and magnitude of the second peak. The peak magnitude of sodium silicate activated MK at 60°C is 4.3 and 12.8 times of its 40°C and 30°C counterpart, respectively. In addition, the time needed to reach the summit of the second peak is significantly shortened. Similar with the FA geopolymer, the cumulative heat release is significantly influenced by reaction temperature. The increment of total heat release of the MK geopolymer caused by temperature increase is much lower than of the FA geopolymer, demonstrating more serious temperature dependence of the latter.

The isothermal calorimetry heat correlates well with the formation of reaction products [19]. Extensive efforts have also been made to predict the early age strength of resultant cement concretes and mortars [27,28]. These studies demonstrated that the isothermal calorimetric information can be used to decide about the initial curing procedure. Table 5 summarizes the cumulative heat release properties of both geopolymers. For both reaction systems, most of the measured heat was released within the first 12 or 24 h. Thus, the 12 and 24 h were adopted as the preliminary heat treatment duration in the following part. Higher reaction temperature and extended treatment periods are not considered in this work, because both will consequently curtail the environmentally friendly property of geopolymer.

3.2. Mechanical properties

Fig. 4 depicts the flexural and compressive strengths of FA and MK geopolymer mortars initially cured under different conditions. For both materials, increasing initial curing temperature contributes to the development of early age mechanical strength. The rate of strength gain of FA based geopolymer is more significant than its MK counterpart, once again demonstrating the temperature dependence of the alkali activation of FA. Compared with the effect of 30°C and 40°C treatment, the influence of 60°C curing on strength development is more notable.

In addition, extending the duration of elevated curing temperatures also promotes the strength gain of FA geopolymer. The 3 d compressive strengths of samples cured at 60°C for 12 h and 24 h are 8.8 and 13.5 times of samples initially cured at 20°C , respectively. As aforementioned and reported in other studies [29,30], the dissolution and gelation of FA based geopolymer is minute at room temperature because of the low reactivity. Elevated temperature treatment is necessary during the incipient stage to overcome the energy barrier. In contrast, the high reactivity of MK results in the fast geopolymerisation even at ambient

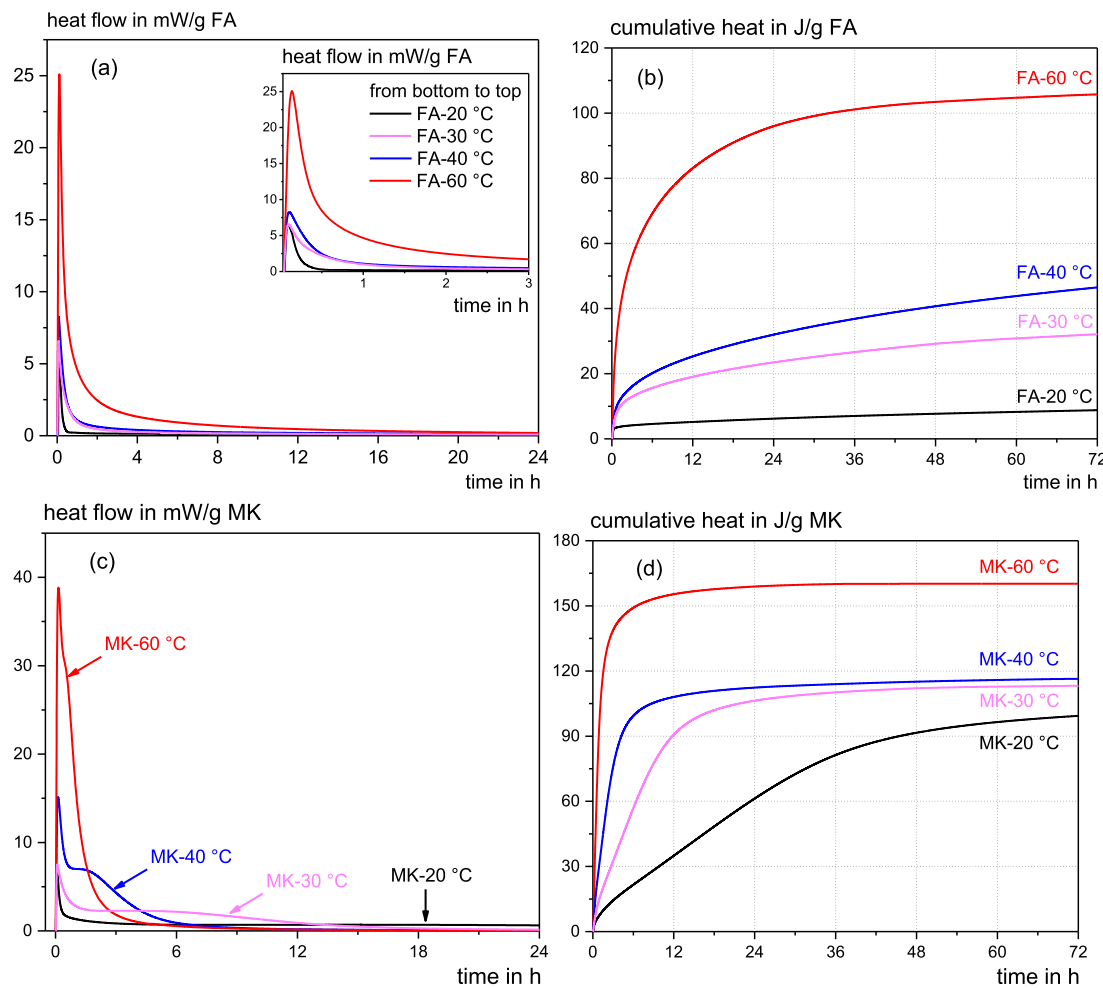


Fig. 3. Effect of reaction temperature on heat evolution of FA and MK geopolymers.

Table 5

Heat release properties of FA and MK geopolymer.

Temperature	FA Geopolymer			MK Geopolymer		
	Q_{72}^a (J/g)	Q_{12}/Q_{72}^b	Q_{24}/Q_{72}	Q_{72} (J/g)	Q_{12}/Q_{72}	Q_{24}/Q_{72}
20 °C	9.0	0.58	0.69	99.7	0.35	0.68
30 °C	32.1	0.59	0.73	113.2	0.80	0.94
40 °C	46.6	0.54	0.69	116.3	0.93	0.97
60 °C	105.8	0.78	0.91	159.7	0.97	0.99

Q_{xx} : the cumulative heat release of xx h.

Q_{xx}/Q_{72} : ratio of Q_{xx} to Q_{72} .

condition.

As the age increases, the strength of elevated temperature treated FA geopolymers gradually increased and approached a maximum of approx. 63 MPa. In comparison, the sample initially cured at 20 °C stood out after 96 days and achieved the highest strength afterwards. The one year flexural and compressive strengths of FA-20 °C are 10.9 MPa and 71.4 MPa, respectively.

For the MK geopolymers cured under different conditions, the mechanical properties are comparable within the investigated period. But it can be inferred that the MK-20 °C possessed a slightly higher final strength than the others, which is similar with the FA system. It is supposed that high temperature treatment favours the dissolution of solid precursor and formation of reaction products, which contributes to the early age strength development [21]. Meanwhile, the enhanced reaction has negative effects on the microstructure and quality of

reaction products. As Puertas et al. [31] stated that diffusion is a rate-determining step of high temperature geopolymerisation, resulting in the aggregating of reaction products close to the precursor grains. This may gradually cause an inhomogeneity in the microstructure and lower the continuous reactions during aging [32].

It should be mentioned that a strength reduction after 28 days has been reported by several researches [11,33,34]. Further comparison with these results will be conducted to reveal the significance of gel chemistry on long-term behaviours of geopolymers.

3.3. Pore structure

The MIP test was carried out to analyse the pore structure of geopolymer mortars produced in this work. The main purpose of applying the MIP measurement is to compare the pore size evolution during geopolymerisation. Part of the measured results are presented in Fig. 5 to show the trend, and details about the porosity and median radius are summarized in Table 6.

As shown in Fig. 5, both geopolymer systems predominantly consist of pores less than 1 μm . According to Mehta and Monteiro [35], these pores can be divided into gel pores (< 0.01 μm) and capillary voids (0.01–1 μm). The volume and size of the capillary voids are determined by the liquid-to-solid ratio and the reaction degree. The porosity and median radius in FA-20 °C are high at the early ages, indicating the low reaction degree. It can be inferred from Fig. 5 and Table 6 that the total porosity and median radius decrease during aging. The gradual formation and coagulation of reaction products can fill the large voids

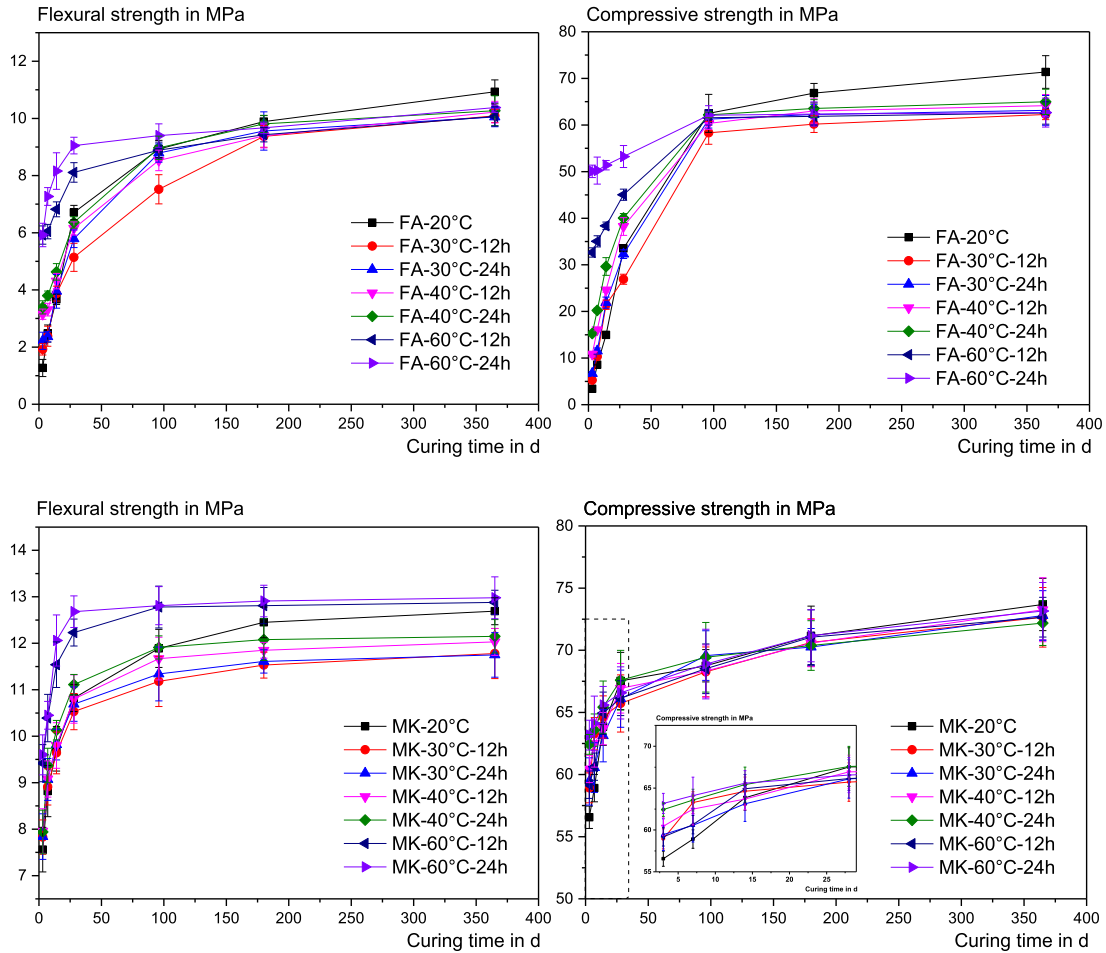


Fig. 4. Flexural and compressive strengths of FA and MK mortars.

[32], leading to the pore size shift. Capillary voids larger than $0.05\ \mu\text{m}$ are reported to be more influential in determining the strength property of cementitious materials [35]. Thus, the decrease of pore size of FA samples cured and aged at 20°C contributes to the significant strength increase discussed above. In contrast, due to the accelerated reaction in 60°C cured FA geopolymer system, the pore size shift is less obvious than at 20°C . This supports the above discussion that fast reaction and hardening process results in worse pore characteristic.

The MK geopolymer system showed very slight change in porosity and median radius during aging, regardless of the initial reaction

temperature. This can be assigned to the fast geopolymerisation, which contributes to the rapid formation of hardened structures. The similar pore size property of MK geopolymers initially cured at 20°C and 60°C are supposed to be responsible for the only slight variation in strength. Compared with the FA geopolymer, the MK samples possess higher porosity and much smaller median radius. The high porosity is caused by the high liquid to solid ratio during geopolymer preparation. The median radius of MK system indicates that the pores are mainly composed of smaller capillary voids and interparticle spacing between the N-A-S-H sheets [3,35].

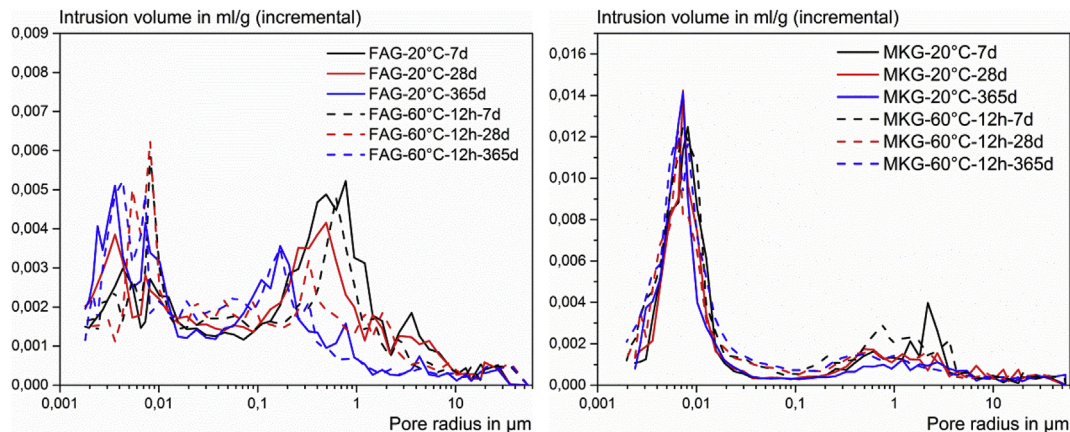


Fig. 5. Pore size distribution of FA and MK geopolymer mortars.

Table 6
Pore size properties of FA and MK geopolymer mortars.

Sample ID	Total porosity, in %	Median radius, in μm
FA-20°C-7d	23.53	0.3109
FA-20°C-28d	20.18	0.2315
FA-20°C-180d	16.61	0.1018
FA-20°C-365d	15.82	0.0881
FA-60°C-12h-7d	18.61	0.2214
FA-60°C-12h-28d	17.74	0.1619
FA-60°C-12h-180d	17.09	0.1231
FA-60°C-12h-365d	16.68	0.0915
MK-20°C-7d	28.91	0.0072
MK-20°C-28d	26.49	0.0062
MK-20°C-180d	27.06	0.0060
MK-20°C-365d	25.82	0.0054
MK-60°C-12h-7d	29.14	0.0081
MK-60°C-12h-28d	28.03	0.0077
MK-60°C-12h-180d	26.92	0.0078
MK-60°C-12h-365d	25.11	0.0076

3.4. Reaction products

Fig. 6 depicts the XRD patterns of FA and MK geopolymers of different ages, more detailed information can be found in Fig. S1. Most of the minerals from the solid precursors remain unchanged except the anhydrite in FA and illite in MK. The reflection peaks of anhydrite and illite gradually decreased, demonstrating the dissolution of these phases in the high pH environment. The dissolution rate varies, peaks of anhydrite cannot be detected after 7 days even at 20 °C, while traces of illite can still be found after one year. For both geopolymers initially cured at different conditions, a shift of the amorphous hump to higher 2 θ angles can be seen in Fig. 6. This phenomenon indicates the

formation of new amorphous phases, which is a highly cross-linked, structurally disordered N-A-S-H [1,3]. Increasing initial curing temperature and aging time enhanced the pattern shift, illustrating the increased geopolymerisation degree. This favored the continued strength development and densified structure of the resultant geopolymers.

For FA geopolymer initially cured at 20 °C, new reflections at 24.34°, 34.42° and 37.48° 2 θ , can be attributed to the formation of cancrinite ($\text{Na}_8(\text{Si}_6\text{Al}_6\text{O}_{24})(\text{H}_{0.88}(\text{CO}_3)_{1.44})(\text{H}_2\text{O})_2$, PDF No. 98-001-8104). Apart from cancrinite, not well crystallized franzinite ((Na, Ca) $_7(\text{Si}, \text{Al})_{12}\text{O}_{24}(\text{SO}_4, \text{OH}, \text{CO}_3)_3\text{H}_2\text{O}$, PDF No. 00-030-1170) was also detected in FA geopolymer samples initially cured at 40 °C and 60 °C. Reflections of levyne ($\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12})\cdot 6\text{H}_2\text{O}$, PDF No. 00-011-0582) can be seen in Fig. 6 (b), around 9.07°, 17.21°, 29.06° and 51.45° 2 θ in 60 °C cured FA geopolymer. Cancrinite, franzinite and levyne all belong to the ABC-6 zeolite family [36,37]. Their framework is characterized by a basic structural layer containing six-membered rings of Al- and Si-tetrahedral [38]. As shown in Fig. 7, if the position of the rings on one layer is titled A, the two other possible alternative positions in the adjacent layers are called B and C. The notation of this kind of zeolite is described by the stacking sequence of the closest-packed structures. The stacking sequence of cancrinite, franzinite and levyne is AB, ABCABA-CABC and AABCCABBC, respectively [36,37]. Characteristic of this zeolite structure will be discussed in the following FTIR part. Formation of ABC-6 zeolites has also been detected in other studies using fly ash or metakaolin-slag mixture as solid precursors for geopolymer synthesis [36,39,40].

For the metakaolin based geopolymer, no crystalline phase has been detected in samples initially cured at 20 °C and 40 °C. But further increasing the initial curing temperature to 60 °C contributes to the formation of zeolite P1 ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$, PDF No. 00-044-0103).

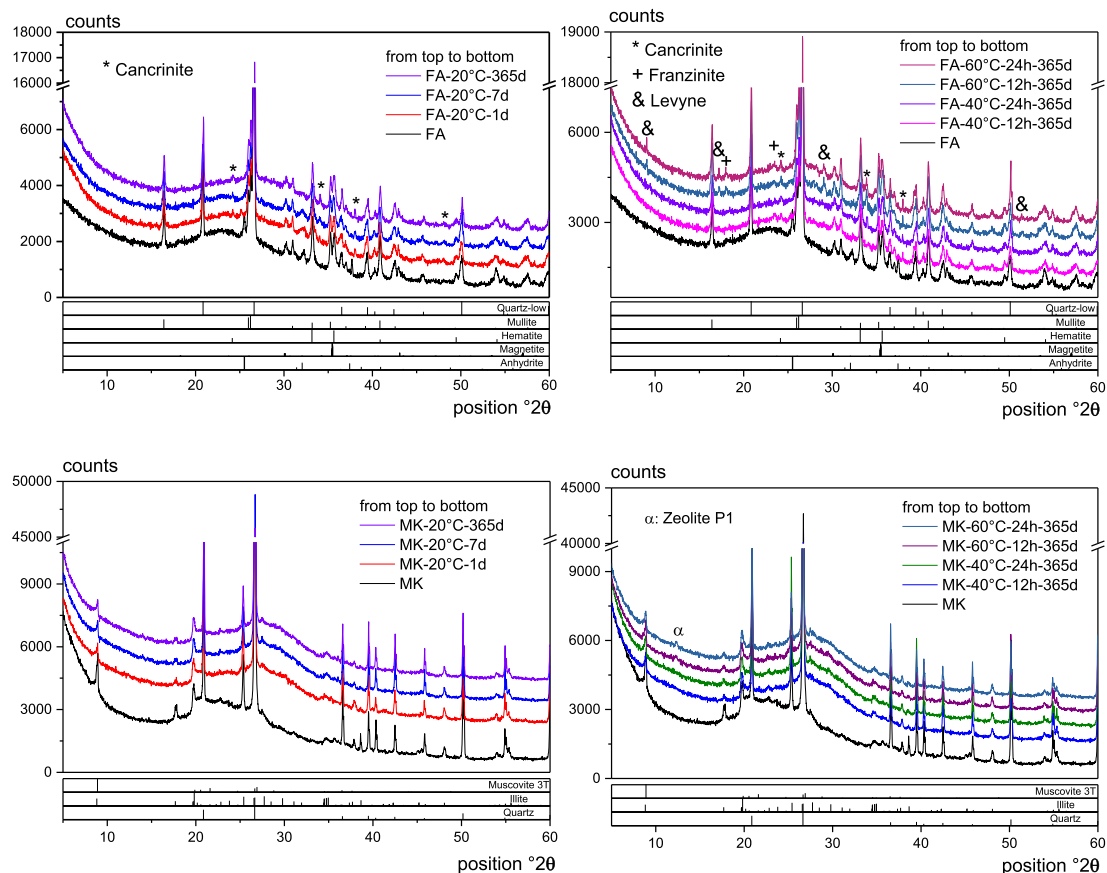


Fig. 6. XRD patterns of FA and MK geopolymers.

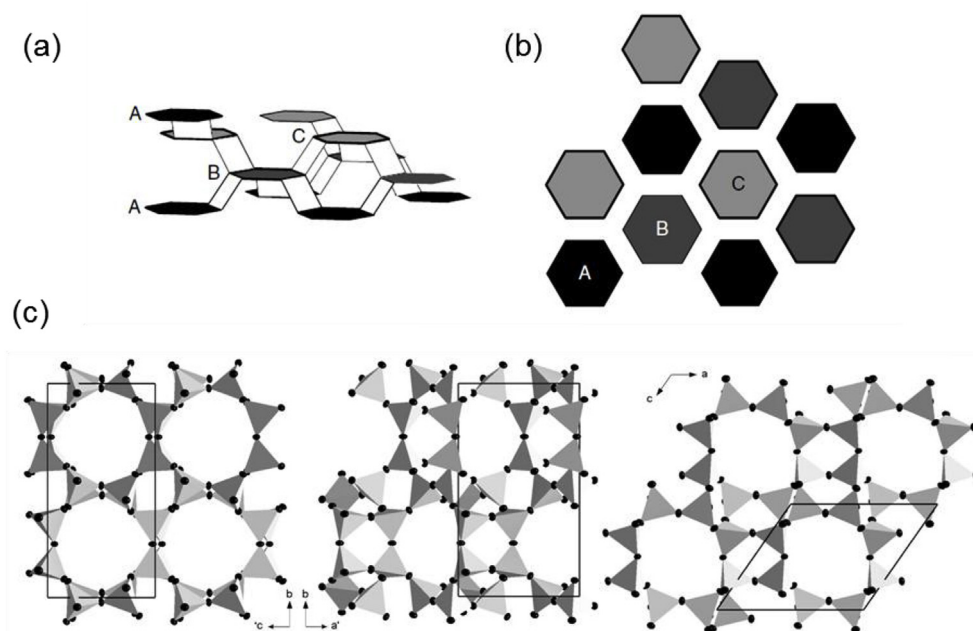


Fig. 7. Stacking of hexagonal arrays in ABC-6 zeolites viewed from (a) the side and (b) in projection [37], and (c) schematic framework of phillipsite viewed along [100], [010] and [001] [41].

The topology of zeolite P1, shares the structure of phillipsite (Fig. 7 (c)), which consists of two sets of doubly connected 4-membered rings linked into double crankshaft chains [4,11].

The identification of zeolite phases in geopolymeric materials is not unexpected. Studies have stated the similarity between geopolymerisation and zeolite formation, except that zeolite is usually synthesized at higher temperature and water content [4,42,43]. The rate of zeolitic nucleation in a given system depends on many factors, such as temperature, supersaturation degree of solution, presence of nucleation triggers, etc [2,7]. The fast formation of cancrinite in FA geopolymer demonstrates that the nucleation rate is high. In our previous study [19], cancrinite was formed after 0.5 h of mixing NaOH with fly ash, this period roughly equals the concentration accumulation of dissolved ions. In addition, quick forming of zeolite phase indicates that the on-site of zeolite formation in this work is a simultaneous process with geopolymerisation. This is further supported by phases generated at elevated temperature. The franzinite, levyne and zeolite P1 were detected in samples initially cured at 40 °C or 60 °C, but not in the 20 °C cured counterpart even after one year. In spite of the hydrothermal condition required for the formation of these phases [41,44], reflections of these phases were detected at an early age (Fig. S1). It can be supposed that crystalline seeds were formed during the initial curing period and then gradually grow up or coagulated during aging.

The authors do not exclude the formation of zeolite or other crystallisation process via consecutive crystallisation of geopolymeric gels. This normally takes place during the secondary heat treatment of hardened geopolymeric materials, for example the accelerated aging of geopolymers investigated by Lloyd [11]. Conclusions of these investigations will not be repeated in detail here.

It should be mentioned that both franzinite and levyne are Ca-bearing. CaO at levels above 3–5 wt % with respect to the amorphous aluminosilicate have been observed to interfere with the formation of zeolites [45]. Meanwhile, according to Provis et al. [7], nucleation and crystal growth of zeolites were not prevented in this kind of reaction system. Formation of Ca-bearing zeolites has also been observed in other reported studies [36,46]. In addition, the role of CaO during geopolymerisation is one of the current research focuses [15,47–51]. Coexistence of C-A-S-H and N-A-S-H has been detected in alkali activated materials with medium calcium content [47]. For those with

calcium-poor formulation, calcium modified N-A-S-H gel ((N,C)-A-S-H, in abbreviation) was observed by Garcia-Lodeiro et al. [47]. via studying the compatibility of N-A-S-H and C-A-S-H gels. The formulation of FA geopolymer synthesized in this work meets condition ($0 < \text{Na}_2\text{O}/\text{Al}_2\text{O}_3 < 1.85$, $0 < \text{CaO}/\text{SiO}_2 < 0.3$) for the formation of this (N, C)-A-S-H gel. Whether the calcium participates in the geopolymeric gels obtained in this study will be checked in future investigations.

3.5. Fourier transform infrared spectroscopy (FTIR)

To obtain a better understanding of the chemistry of FA and MK geopolymers, a detailed study of the FTIR was conducted, taking the initial curing temperatures and ages into account. As shown in Fig. 8, substantial changes can be seen in the range of 400–1700 cm^{-1} and around 3500 cm^{-1} . To gain a better view of these features, the analysis will focus on four regions (see Fig. 8 Fig. 9 and Fig. 10): (a) bands between 400 and 800 cm^{-1} ; (b) T-O (T = Si or Al) bands at about 850–1250 cm^{-1} ; (c) vibration bands of the CO_3^{2-} groups; and (d) OH stretching and deformation bands centred around 1650 cm^{-1} and 3500 cm^{-1} .

3.5.1. Bands between 400 and 800 cm^{-1}

This region mainly contains vibration bands generated by inter-linked SiO_4 and AlO_4 tetrahedra [39]. These units form rings of different numbers of members and give rise to super-tetrahedral material of medium range order [49]. As shown in Fig. 9, both unreacted FA and MK give similar FTIR spectrum in this region. The signal centred at 450–470 cm^{-1} corresponds to the internal deformation vibrations of the T-O bond [21]. The band appearing at 560 cm^{-1} and the shoulder around 610 cm^{-1} (only in FA system) are correlated with the symmetric stretching vibration of 4-membered rings [52]. During the geopolymerisation, the intensity of this 560 cm^{-1} band first decreased and then increased. This phenomenon is more observable in the specimen initially cured at 20 °C. This transformation implies the dissolution of solid precursors and formation of new phases. Bands locating in the range of 650–800 cm^{-1} are assigned to the stretching modes primarily associated with the motions of Si or Al atoms [39]. Those in the lower spectral region of 650–720 cm^{-1} can be further classified as the

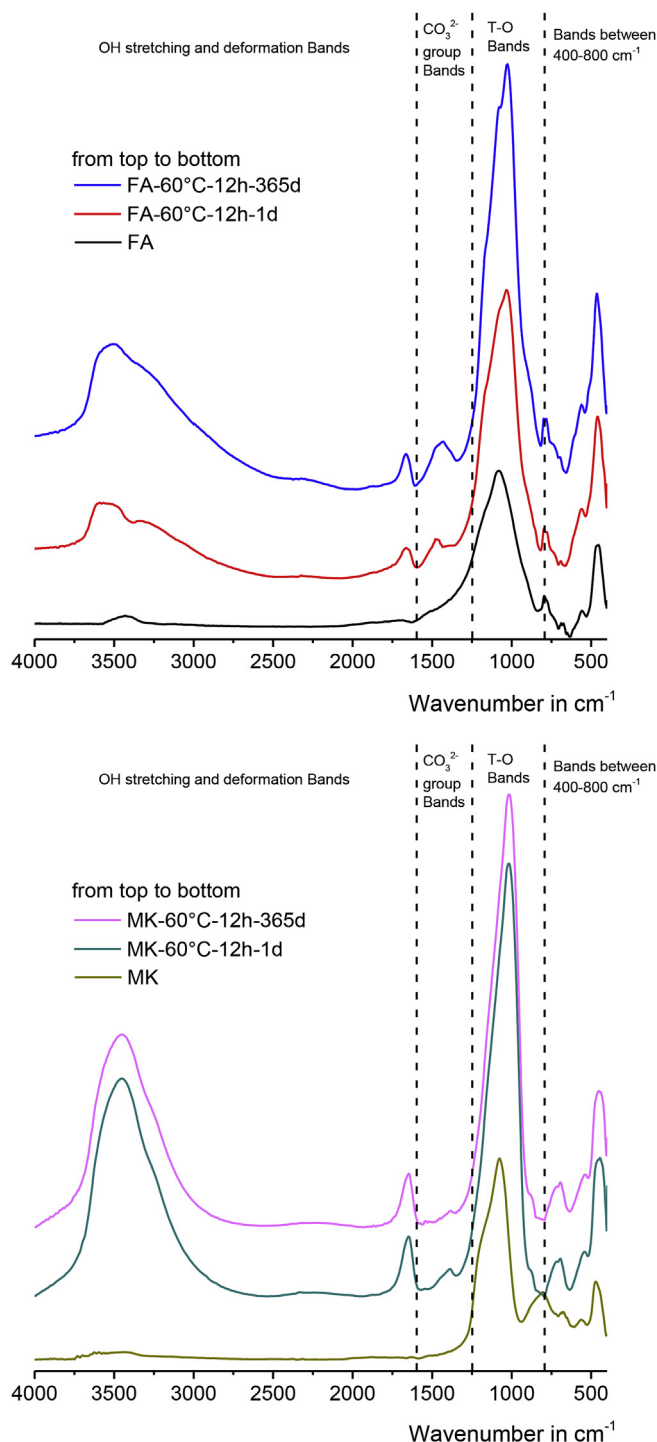


Fig. 8. Overview of the FTIR spectra of the FA and MK geopolymers.

internal tetrahedral stretch, while the others in the higher region are assigned to the stretch reflecting structure-sensitive external linkages [40,52]. According to Criado et al. [21,53], the band of 689 cm^{-1} in both FA and MK represent the quartz in the solid precursors, the same applies for the 790 cm^{-1} band in FA. The relative intensity of the quartz band remained unchanged. This is consistent with the XRD results that the quartz did not undergo geopolymerisation. The broad band centring around 800 cm^{-1} in the MK can be assigned to the Al–O bending mode of AlO_4 tetrahedral groups [54]. This band was significantly dissolved during geopolymerisation, indicating the breakdown of the original structure.

3.5.2. T-O bands at about $850\text{--}1250\text{ cm}^{-1}$

The T-O bands are predominantly caused by the Si–O(T) stretching vibrations in SiO_4 tetrahedra [53,54]. A shift of the principal band localised around 1000 cm^{-1} to lower wavenumbers can be seen in both geopolymers after reaction. This is indicative of the formation of a gel-type aluminosilicate [53–55]. The shift of this main band towards lower wavenumbers also indicate an increase of band length, decrease of band angle and reduction of the molecular vibrational force constant [56]. Several reasons are responsible for this change, such as the increase in the proportion of silicon with non-bridge oxygens or the substituted amount of tetrahedral aluminium in the silicate network [53,56]. Numerous studies have been published discussing the band shift in this region during geopolymerisation [3,53,54]. In our ongoing work, deconvolution of the spectra in this region is correlated with the quantitative XRD results and evolution of mechanical properties to quantify the long term kinetics of geopolymerisation.

It should be pointed out that, apart from the abovementioned T-O bands, vibration of CO_3^{2-} ($\sim 876\text{ cm}^{-1}$) has also been detected in FA geopolymer in this region. This is discussed in the CO_3^{2-} bands section. According to Zhang et al. [54], the band around 870 cm^{-1} detected in MK geopolymer system represents the unreacted metakaolin.

3.5.3. Bands of the CO_3^{2-} groups

The band at about 876 cm^{-1} in FA geopolymers (Fig. 10) is assigned to CO_3^{2-} group in cancrinite [38,57]. During the aging, this weak but well resolved band gradually evolved into an un-sharp shoulder. This is caused by the low band intensity, which easily interfered by the high intensity T-O vibration bands centring nearby. As discussed in the XRD part, the crystal structure of cancrinite is built up of interconnected six-membered tetrahedral rings, which contain a large 12 membered ring (12 mR) channel [38]. The ϵ -cages (cancrinite-cages) locate around the 12 membered rings. The CO_3^{2-} group, together with cations (K^+ , Na^+ and Ca^{2+}), anions (SO_4^{2-} and Cl^-) and water molecules, lie in the large 12 mR channels and the ϵ -cages [38]. The early and effective detection of this band supports the XRD results that zeolitization is a simultaneous process with geopolymerisation in this work. Considering the similar chemical and micro-structural properties of franzinite with cancrinite, CO_3^{2-} based extra-framework constituent in franzinite may also contribute to the rise of this band.

Bands in the $1300\text{--}1550\text{ cm}^{-1}$ region in both geopolymers are correlated with the anti-symmetric stretching mode of the CO_3^{2-} group [39,58]. These bands are generated via the reaction of geopolymer with CO_2 from the air. Though all samples were wrapped by PE-foil and stored at 20°C and 65% RH condition, contact with CO_2 during sample handling and aging could not be prevented completely. The adsorption and reaction of geopolymer with CO_2 are minute in this work, as shown in the XRD (no carbonate phase was found). Two individual bands can be observed in FA and MK geopolymers cured at 20°C in early age. Na_2CO_3 contributes most to the vibration band centring at 1480 cm^{-1} [39,55]. The Na_2CO_3 is formed via the reaction of CO_2 with mobile alkalis. This is predominant during the early age due to the low reaction degree. Beyond this process, molecular CO_2 can also be adopted and gradually bound to framework oxygen atoms, reflecting as the bands localised around 1400 cm^{-1} [59]. Though attribution of this region as sodium bicarbonate band has been reported [60], formation of bicarbonate product in this work is scarcely possible because of the limited contact of the sample with air. The formation and conversion of carbonates to bicarbonates in accelerated carbonated AAMs have been reported in Refs. [18,61–63]. According to Bernal et al. [18,61], the stability of different Na-carbonate phases depends strongly on the accelerated carbonation conditions. A CO_2 concentration exceeding 0.2% is normally required for the formation of sodium bicarbonate. A potential process responsible for the bands around 1400 cm^{-1} herein could be that the CO_2 molecules were initially adsorbed on charge-balancing Na^+ cations in linear form [59]. The adsorbed CO_2 molecules undergo nucleophilic attack by basic framework oxygen atoms and

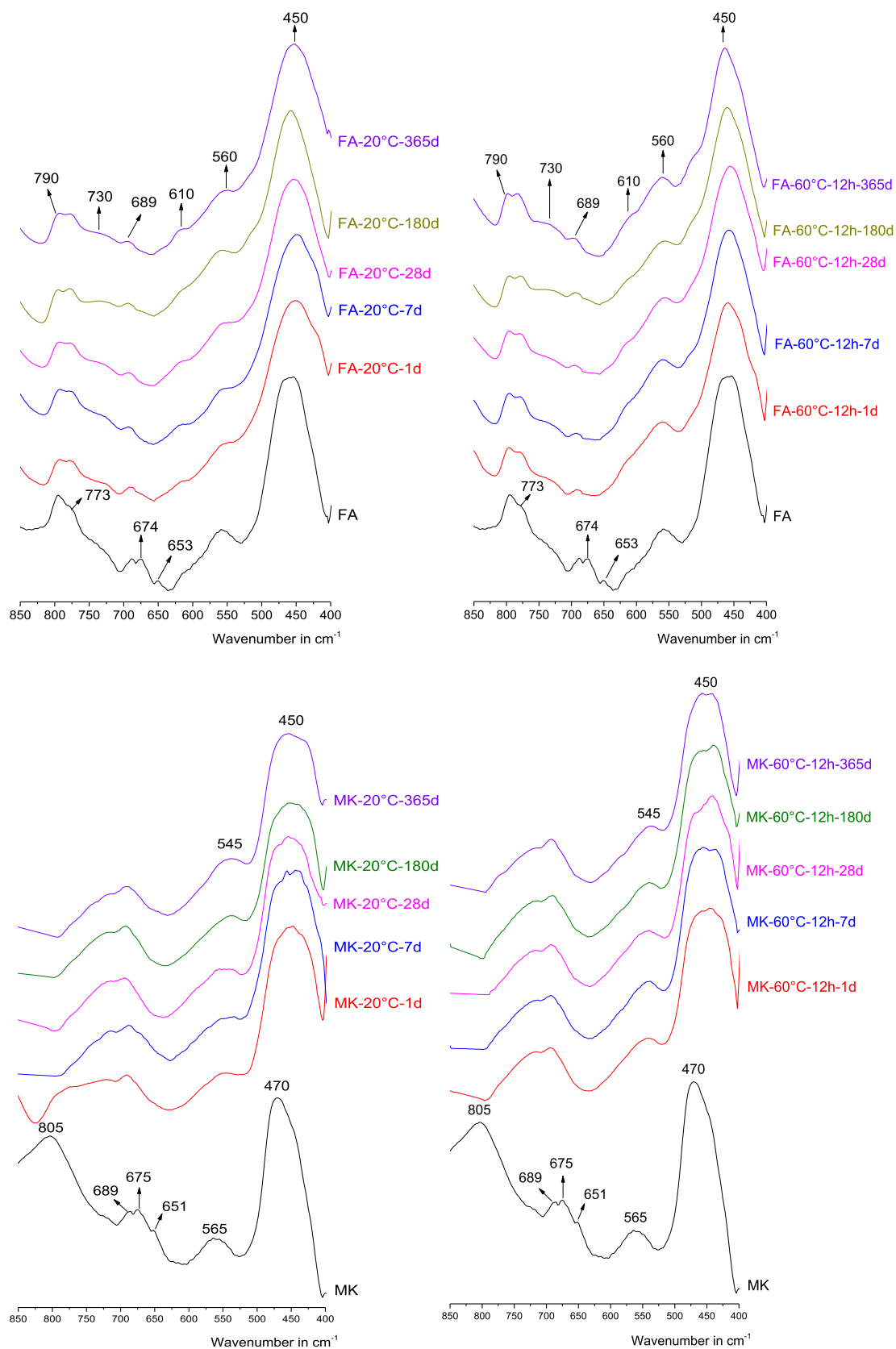


Fig. 9. FTIR spectra of the FA and MK geopolymers ($400\text{--}850\text{ cm}^{-1}$).

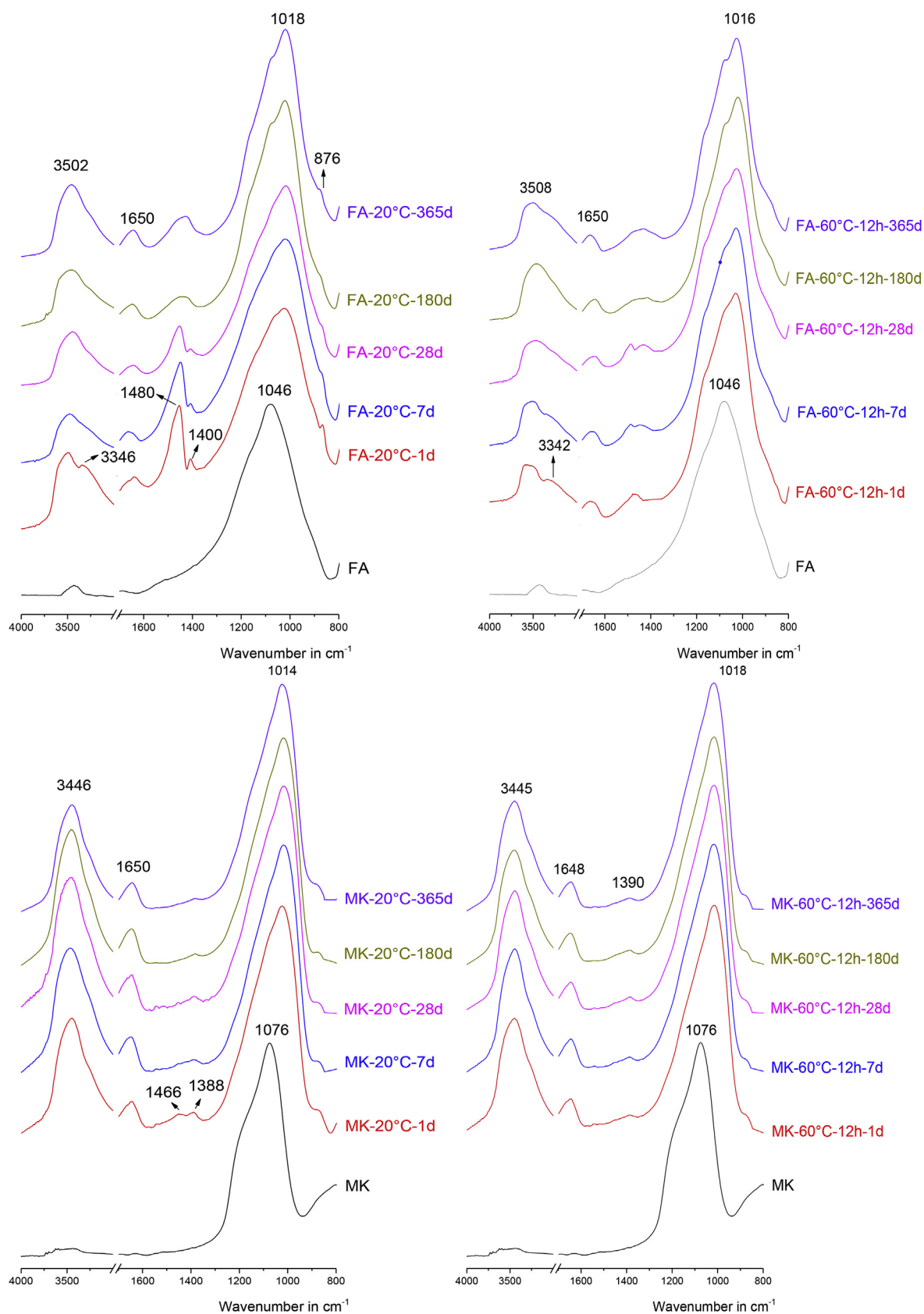
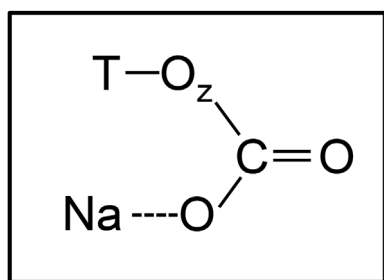


Fig. 10. FTIR spectra of the FA and MK geopolymers ($800\text{--}4000\text{ cm}^{-1}$).



T: tetrahedrally coordinated Si or Al,

O_z: oxygen atom of the framework.

Fig. 11. Schematic structure of carbonate formed via the reaction of CO₂ with framework oxygen (Reproduced from Ref. [59], ©1999, Springer).

form the structure shown in Fig. 11. Numerous aluminosilicate zeolites have been reported to form this carbonate structure after reaction with CO₂ at ambient temperature and pressure [58,59,64]. A more detailed discussion of the chemistry, structure and amount of these carbonate species is planned with a combination of Nuclear Magnetic Resonance spectroscopy.

3.5.4. OH stretching and deformation bands

The wide and intense bands around 3500 cm⁻¹ together with a shoulder at about 3350 cm⁻¹ are assigned to the OH stretching, and the well-defined band at 1650 cm⁻¹ is correlated with the H–O–H deformation [39,54,55]. These bands in the geopolymer samples are generally attributed to the presence of hydrated compounds with constitutional water tightly bound to the molecular structure. According to Beta et al. [65], the band at about 3500 cm⁻¹ can be further accredited to the hydrogen bonded water molecules without phase correlation. In contrast, the one around 3350 cm⁻¹ represents water bonded to specific sites, such as the zeolite [51]. The 1650 cm⁻¹ band indicates the symmetric bending mode of water molecules, which are hydrogen bonded to the isolated non-interacting surface silanol groups [53].

4. Summary and conclusion

In this work, the mechanical and chemical property evolution of sodium silicate activated FA and MK geopolymers are qualitatively studied in a time scale of one year. The effects of initial curing conditions are taken into consideration, which are decided based on the reaction heat property. Following conclusions can be drawn:

- (1) The reaction temperature has considerable influence on the heat evolution of FA and MK geopolymers. Increasing temperature significantly enhances the cumulative heat release of both reaction systems, especially for the FA geopolymer.
- (2) Initial heat treatment contributes to the development of early age mechanical strength of both geopolymer. The strength gain of FA based geopolymer is more significant than its MK counterpart, indicating the temperature dependence of alkali activated FA.
- (3) The strength of elevated temperature treated FA geopolymers gradually increased to reach maximum during aging. In comparison, samples initially cured at 20 °C stood out after 96 days and achieved the highest strength afterwards. For the MK geopolymers initially cured under different conditions, the mechanical properties are comparable within the investigated period.
- (4) Due to the rapid formation of hardened structure, the pore structures of MK samples and heat treated FA geopolymer are almost built at an early age. After 365 d, the ambient cured samples are of lower porosity and the pores are of smaller median radius than those initially cured at elevated temperatures.
- (5) Heat treatment not only promotes the geopolymerisation of both

systems, but also contributes to the formation of zeolite phases. These phases are rapidly formed, indicating that zeolite formation is part of the geopolymerisation process.

- (6) Adsorption and reaction of geopolymer with CO₂ are inevitable during sample handling and aging, resulting in the slight natural carbonation of the geopolymer. Two different carbonation processes are detected: reaction of CO₂ with mobile alkalis, and the adoption and reaction of CO₂ with framework oxygen atoms. The former procedure is predominant at the early age, the latter takes place slowly but continues along aging.

Apart from the above findings, further attention will be paid to the quantitatively analysis of the long-term reaction kinetics. And cross-checking with other state-of-the-art techniques is needed to optimise the study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cemconcomp.2018.10.014>.

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Supplementary data:

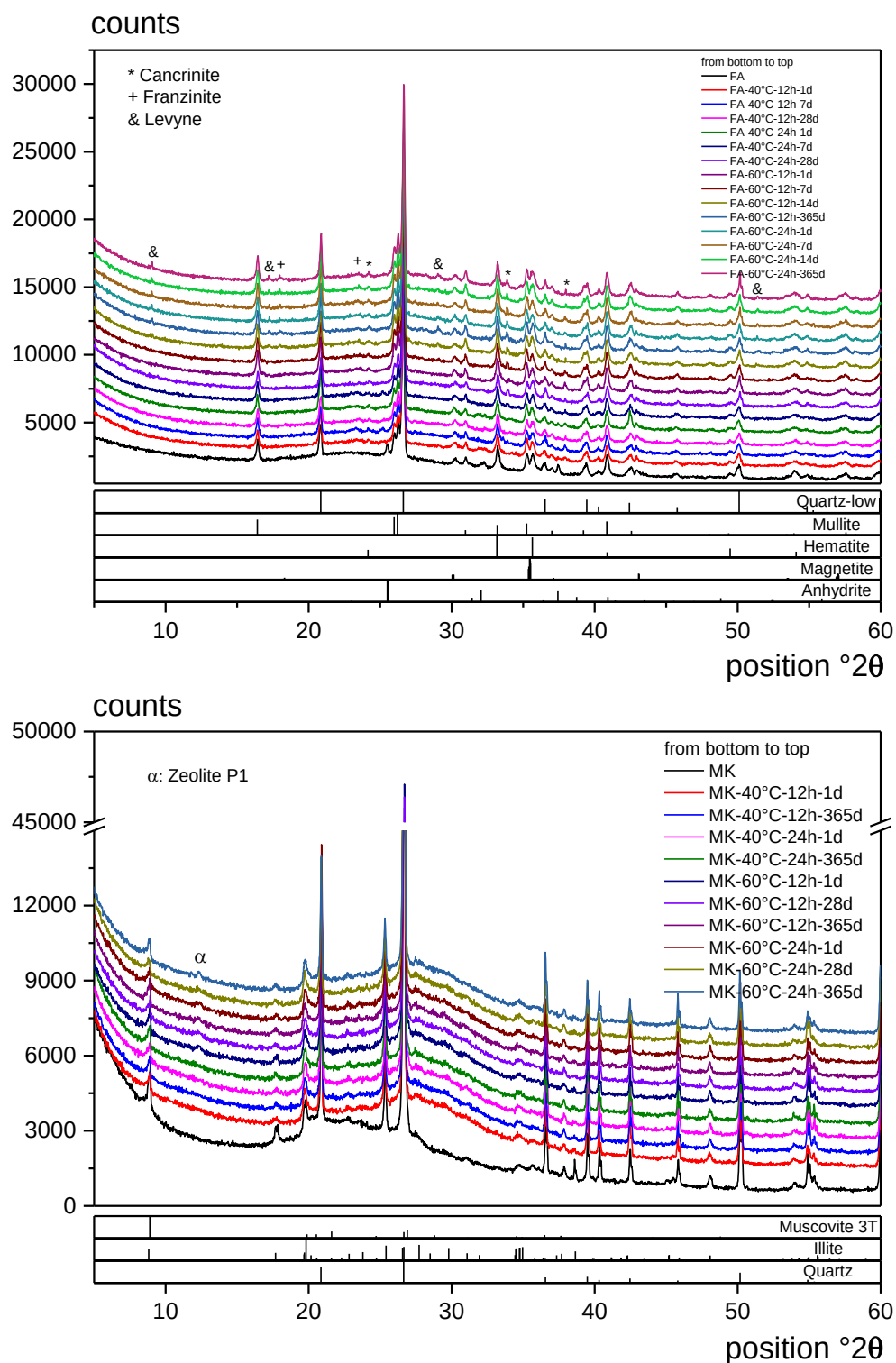


Fig. S1 XRD pattern of FA and MK geopolymer under different initial curing conditions



pH dependent leaching characterization of major and trace elements from fly ash and metakaolin geopolymers



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ABSTRACT

The leaching characteristics of Cl^- , SO_4^{2-} , Na, K, Al, Si, Ca, Mg, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sr, Tl, V, Zn from fly ash and metakaolin geopolymer mortars were characterized in a broad pH range (1–14) in this work. Apart from revealing the partitioning of chemical species between the solid and aqueous phase, the acid neutralization property of both geopolymers were studied. In contrast with the virtually pH independent characteristic of chloride and sulfate, the leaching of the other elements showed pH dependent features, which can be further divided into amphoteric, cationic and oxyanionic patterns. Formation of montmorillonite and amorphous silica were detected by X-ray diffraction after the leaching. The leaching results and mineralogical measurement were coupled with geochemical modelling to identify the solubility controlling phases of Al, Si, Ca and Mg.

1. Introduction

Nowadays, an urgent need is arising for the development and commercialization of alternative cement-like binders because of the high energy consumption and CO_2 emission properties of cement production. Geopolymer is reported as a high-profile example of alternative binders with reduced CO_2 footprint. The term ‘geopolymer’ was coined in the 1970s by the French scientist Joseph Davidovits [1], which refers to a group of low-calcium materials synthesized by alkali activation of aluminosilicates [1,2]. Siliceous fly ash (FA) and metakaolin (MK) are the most extensively used solid source materials, with the most commonly used alkali activators being sodium hydroxide, sodium silicate and their mixtures [3]. The reaction process is complex and normally simplified as dissolution of reactive components from solid precursors, gelation of dissolved ions, polymerization and condensation of gels [1,2,4]. The main reaction product is a structurally disordered alkali aluminosilicate gel (often represented as N-A-S-(H)), in which both silicon and aluminium are in tetrahedral coordination [5,6]. Duxson et al. [6] reported that substitution of silicon by aluminium can take place within N-A-S-(H) framework, with alkali cations balancing the associated negative charges. Similarities between N-A-S-(H) and the structure of zeolites have been reported [7,8]. Provis et al. [7] proposed that the geopolymer gel is fundamentally zeolite-like in chemistry but lacks long-range crystalline order.

Studies about the environmental benefits of geopolymers have been conducted by many researchers (e. g. [9,10]). In comparison with ordinary Portland cement (OPC) concrete, geopolymer concrete can reduce CO_2 emission up to 90% [2,4]. In addition, geopolymers are reported to possess superior engineering properties, such as high early strength, thermal and fire resistance, stability under chemical attack, strong adhesion to metallic and non-metallic surfaces, low permeability to fluids and chloride ions, etc. [4,11]. Each of these benefits is certainly achievable by tailoring mix design, synthesis and curing procedures.

Benefiting from these superior properties, application of geopolymer can range from hazardous/nuclear wastes immobilization to high-volume infrastructure construction. Immobilisations of toxic and nuclear wastes in geopolymers have been well documented in [2]. High-volume concrete constructions based on alkali-activated binders, including a 4 story high building and an airport, have been constructed in Australia. These applications generate confidence in these kinds of concrete, but also raise concerns about the long-term mechanical, structural and environmental behaviour of geopolymers. The environmental credits of geopolymer should not only include the CO_2 emission, but also the leaching of different elements when it comes in contact with water.

Solid precursors for geopolymer synthesis are often industrial wastes or by-products, which contain different amounts of toxic

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elements. Geopolymers synthesized using these wastes or by-products possess the potential of bringing contaminations into the environment. Laboratory leaching has been conducted by different authors while immobilizing hazardous materials and radioactive wastes using geopolymer, but all these studies focus on the leaching of artificially supplied toxic elements [12–14]. In addition, geopolymer matrixes used to solidify hazardous material are meant to be deposited, rather than being used as building materials. The permissible release on a deposit is much higher. With the increasingly stringent environmental regulatory criteria for building materials, the leaching behaviour of initially contained heavy metals and trace elements from geopolymer-based structural concrete should be fully evaluated before marketing.

Cementitious materials might be exposed to varying external pH conditions at the field site, such as low ionic strength rain fall, acid soil water, waste water etc. Characterizing the leaching behaviours over a broad pH range is fundamental in tailoring the field application of materials. As part of the evaluation framework, pH dependent leaching has been widely applied to evaluate the environmental contamination potential of inorganic constituent from wastes, and primary and secondary building materials [15–17]. In order to develop a reliable pH-dependence test, Dijkstra et al. [18] investigated the influence of time on the chemical equilibrium condition of pH dependent leaching. Results showed that an equilibration time of 48 h is a suitable operational choice because the detected concentrations are close to its 168 h counterpart and modelled results. This equilibration time has been adopted by European standard EN 14429 and American EPA 1313 method. Hence, the suspension is brought towards chemical equilibrium before determining the partition properties of different elements. Engelsen et al. [19,20] and van der Sloot [21] conducted systemic studies on the leaching and chemical speciation of cement concrete, in which the pH leaching is combined with geochemical modelling. The partitioning of chemical species between the solid and aqueous phase were characterized, as well as the assemblages of solubility controlling mineral phases. The modelling results agreed well with experimental measurement. All these investigations not only contribute to better understand the fundamental leaching processes, but also help to predict the leaching under other exposure conditions and to improve the ultimate quality of studied materials. Apart from these solubility studies, further investigations are needed to evaluate the leaching behaviour of monolithic building elements, because the physical binding, especially the diffusion coefficient of the specific material has to be considered. For concretes made of traditional cementitious binders studies focusing on the influences of specific internal or external parameters have been conducted (e. g. [22–24]). However, for geopolymers studies about this aspect have not been reported so far.

In this work, the pH dependent leaching characteristics of major and trace elements from sodium silicate activated fly ash and metakaolin geopolymers are studied, which provides thorough characterization about the partitioning of chemical species between the solid and aqueous phase at different pH values. The acid neutralization capacities of both geopolymers were revealed. Dissolution and formation of mineral phases after the leaching were characterized using X-ray diffraction (XRD). The leaching results and mineralogical evolution were coupled with geochemical modelling to identify the solubility controlling phases of Al, Si, Ca and Mg.

2. Materials and methods

2.1. Materials

The FA and MK used in this work are commercially available materials. Physicochemical properties of the solid precursors have been characterized and reported in [25,26]. Briefly, the Blaine specific surface area value of the FA and MK is 3253 cm²/g and 5397 cm²/g, respectively. The chemical composition was detected using X-ray Fluorescence (XRF). As listed in Table 1, both solid source materials are

Table 1

Chemical composition of FA and MK, see also [25].

Parameter/compound	FA	MK
	wt%	wt%
Loss on ignition	3.27	1.76
Al ₂ O ₃	21.67	32.58
SiO ₂	52.72	61.24
CaO	4.85	0.13
Fe ₂ O ₃	9.55	1.17
MgO	1.89	0.15
P ₂ O ₅	0.48	0.05
TiO ₂	0.90	1.64
MnO	0.08	–
Na ₂ O	1.11	0.17
K ₂ O	2.27	0.63
Na ₂ O-equivalent	2.61	0.58
Sulfur as SO ₃	1.09	0.07
Chloride	0.009	0.010
Carbon	2.30	0.03
Cr ₂ O ₃	0.04	0.02
V ₂ O ₅	0.05	0.03

–: not determined.

mainly composed of SiO₂ and Al₂O₃. Mineral composition was measured by XRD and quantitatively analysed, results are shown in Fig. 1 and Table 2. The high content of amorphous phases in FA and MK indicates high reactivity during geopolymerization.

Table 3 lists the chemical composition of the amorphous phase in FA and MK, which was calculated by subtracting the mineral part from the bulk composition. This can better represent the reactive component contained by FA and MK than using the bulk composition.

The activator used was sodium silicate solution with a modulus of 1.5. The sodium silicate solution contains 23.7 wt% SiO₂, 16.4 wt% Na₂O and 59.9 wt% H₂O. Two geopolymers were synthesized in this work by mixing activator with FA and MK, respectively. The activator-to-solid ratio was 0.45 for fly ash geopolymer (FAG) and 0.75 for metakaolin geopolymer (MKG). This was adopted from our previous studies [25,26]. Compositions of main components in FAG and MKG are listed in Table 4, which were calculated based on the mixing proportion and the chemical composition of amorphous phases in Table 3.

2.2. Sample preparation and pre-treatment

Geopolymer mortars were prepared by mixing weighted solid precursor and activator in a planet mixer. After 2 min mixing, sand was added with the mass ratio of sand-to-binder being 3. Standard sand according to European standard EN 196-1 was used. After another 3 min mixing, homogeneous mortar was obtained and then casted into moulds of 40 × 40 × 160 mm³ and vibrated for 2 min to remove entrained air bubbles. The curing procedure significantly influences geopolymerization process and the property of resultant material. The influence of curing procedure on FAG and MKG has been investigated in our previous work [26]. In brief, the FAG is temperature dependent. Increasing temperature from 20 °C to 40 °C or 60 °C contributes to the development of early age mechanical strength. The effect of heat treatment on MKG is less notable than on FAG. Comparable mechanical properties were achieved by MKG samples initially cured under different conditions. Strengths of both geopolymers continuously increase within the investigated period (one year), but the strength gain gradually slows down. Based on the findings, the curing procedures are developed to produce geopolymers with good early-age and long-term mechanical properties. The FAG samples were sealed in plastic bags and then stored in an oven of 40 °C, the relative humidity (RH) inside the bags is approx. 100%. MKG samples were covered by glass plate over the moulds and stored in curing box of 20 °C and ca. 100% RH. All samples were demoulded after 24 h, wrapped by PE-foil and further

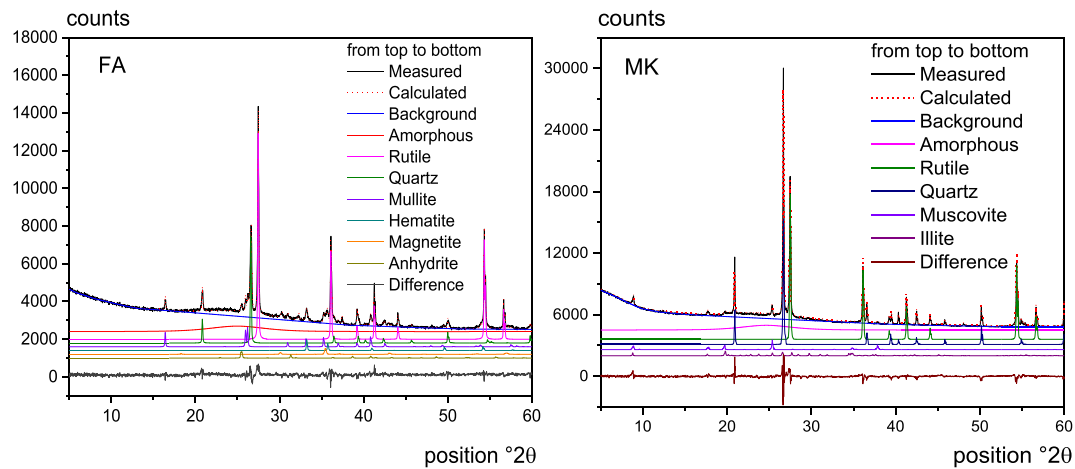


Fig. 1. XRD pattern of FA and MK [25].

Table 2
Mineralogical composition of FA and MK [25].

Phase	PDF-Nr.	FA	MK
		wt%	wt%
Mullite	98-008-0124	9.7	–
Quartz-low	98-005-6873	11.0	–
	98-002-3071	–	12.5
Magnetite	98-007-7842	2.2	–
Hematite	98-010-8081	2.5	–
Anhydrite	98-001-0223	1.4	–
Muscovite 3T	98-003-4922	–	3.3
Illite	98-005-6872	–	1.8
Amorphous	–	73.0	82.4

Table 3
Calculated chemical composition of the amorphous parts in FA and MK [25].

Compound	FA	MK
	wt%	wt%
Al ₂ O ₃	14.4	30.2
SiO ₂	39.1	46.7
CaO	4.2	0.1
Fe ₂ O ₃	4.7	1.0
MgO	1.9	0.1
TiO ₂	0.9	1.6
MnO	0.1	–
Na ₂ O	1.1	0.2
K ₂ O	2.3	0.2
Na ₂ O-equivalent	2.6	0.3
Others	4.3	2.3

Table 4
Molar ratios of the geopolymers systems.

Sample	SiO ₂ / Al ₂ O ₃	SiO ₂ / Na ₂ O	SiO ₂ / (Na ₂ O + CaO)	H ₂ O/ Na ₂ O	H ₂ O/ (Na ₂ O + CaO)
FA geopolymer	5.86	5.14	3.51	9.30	6.35
MK geopolymer	3.62	5.28	5.23	12.27	12.17

cured at 20 °C and 65% RH until an age of 56 days. Samples produced in this procedure possess 28 d compressive strength of 40.1 MPa for FAG and 67.5 MPa for MKG [26], which satisfy most structure application scenarios.

Splitting and size reduction were conducted according to the standards EN 932-2 and EN 15002 using a jaw crusher. Precautions, such as

cleaning the sieves using isopropanol and deionized water, were taken to minimize the risk of contamination. The retained fraction by the sieve was recycled for further size reduction until $\geq 85\%$ of the initial mass was reduced to pass 2 mm sieve. Attention was also paid to make sure that no fine particles were lost during whole size reduction procedure. The crushed particles were used for the potentiometric titration and pH dependent leaching test.

2.3. Potentiometric titration

Potentiometric titrations were conducted to reveal the acid neutralization (buffer) property of FAG and MKG mortars. The obtained titration curve can be used to determine the required amount of acid/base for pH leaching tests. Titration was conducted on suspension of 60 g crushed geopolymer mortar (from section 2.2) mixed with 600 ml deionized water ($> 18.2 \text{ M}\Omega \text{ cm}$). The suspension was continuously homogenized during titration by magnetic stirrer. Mettler Toledo DL50 equipped with titration manager and a high precision auto burette was used. The pH value was simultaneously read using a glass combined electrode. Prior to the experiment, the pH electrode was calibrated using a three-point calibration method (pH 10.00, 7.00 and pH 4.01 at 22 °C). HNO₃ of 1 mol/l was used as titrant. The opening of the vessel was sealed with foil to minimize the influx of air. Based on the obtained titration data, the buffer capacity of geopolymer-mortar suspension was calculated using Eq. (1) [27].

$$\beta = \frac{dC_a}{d(\text{pH}) \cdot m} = - \frac{dC_b}{d(\text{pH}) \cdot m} \quad (1)$$

β buffer capacity of studied suspension, in mol/kg
 m mass of crushed geopolymer mortar, in kg
 C_a amount of acid used, in mol
 C_b amount of base used, in mol.

2.4. pH dependent leaching and chemical analysis

The pH dependent leaching test was conducted following EPA 1313. This method was designed to assess the pH leaching behaviour of inorganic components in terms of equilibrium conditions at different pH values. In this work, 13 suspensions were prepared with pH values ranging from 1 to 14. Each suspension was made of 60 g crushed geopolymer particles and 600 ml deionized water in 1000 ml HDPE vessels. The end-pH value was achieved by adding HNO₃ (Suprapur) or NaOH solution (analytical grade). The required amount of HNO₃ was derived from the titration curve. Due to the initial high alkaline property of geopolymer, one or two pH values higher than natural pH were adopted

to meet the requirements of EPA 1313. The added amount of NaOH was determined by pre-tests. The natural pH is referred to the pH value of suspension without adding acid or base. In addition, to verify that analytic interferences were not introduced as a consequence of reagent impurities or equipment contamination, blank tests without solid samples were carried out. All vessels were tumbled at 8 rpm in an end-over-end roller for 48 h. After that, the pH, redox potential and electrical conductivity were measured. For the measurement of main and trace elements, centrifugation was conducted to separate the solid and the eluate. Concentration of Na, K and Ca were measured using flame photometry (ELEX 6361, Eppendorf), the Cl^- and SO_4^{2-} content were measured by ion chromatography (ICS 1100, DIONEX). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, 5110, Agilent) was used to analysis the concentration of Si, Al, As, Ba, Cd, Co, Cr, Cu, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Tl, V, Zn. Before the ICP-OES measurement, the eluates were acidified with 5 vol% supra pure nitric acid after sampling.

2.5. XRD measurement

Powder XRD measurement was conducted on solid source materials, geopolymers before and after leaching. The measurements on solid precursors have been described in [25,26] in detail. For the measurement of FAG and MKG before leaching, 5 g of crushed particles were manually ground in the agate mortar to $< 63 \mu\text{m}$. Ground fine powder was used for XRD measurement in the theta-theta geometry. Data were collected over the 2θ range of $5\text{--}60^\circ$, and the $\text{CuK}\alpha$ X-rays were generated under 40 kV and 40 mA tube operating condition.

During the centrifugation process, which was used to separate the liquid from the solid phase after leaching, all solid residues were collected and rinsed using deionized water to get rid of the adhered acid or base reagent. Samples were then dried in a vacuum oven at 40°C . Dried samples were ground to fine powders under $63 \mu\text{m}$ for XRD measurement. To confirm that good repeatability was achieved throughout the measurement, the entire procedure of sampling, grinding and measurement was repeated three times.

HighScore Plus, the software from PANalytical, was used to analyse the XRD data, details about the analysis procedure can be found in [25,26].

2.6. Geochemical modelling

Geochemical modelling was carried out to explore the solubility controlling phases of Al, Si, Ca and Mg. The LeachXS (Leaching Expert System) version 1.4.0.1, jointly developed by the Energy Research Centre of the Netherlands (ECN, now ECN for TNO) and Vanderbilt University (Nashville, USA) [28], was applied for data interpretation and geochemical modelling. In addition, LeachXS has incorporated the speciation and transport modelling framework ORCHESTRA. The mineral saturation, solution speciation and sorption processes can then be calculated based on equilibrium models and corresponding thermodynamic data via the ORCHESTRA framework [28,29]. For the highly alkaline systems, an extended version of the thermodynamic database MINTeq2 was adopted. It should be mentioned that the recently updated Cemdata 18 [30] was also incorporated in LeachXS.

The measured data from pH-dependent leaching were used as input in LeachXS. The first step of the modelling was screening the saturation levels of mineral phases that possibly control the leaching of elements. In the model, this is achieved by calculating the ion activity product (IAP) and the given equilibrium constant (K_e). The saturation index (SI) is expressed as $\text{SI} = \log(\text{IAP}/K_e)$. A close to zero SI value (representing the calculated IAP for a specific reaction is close to the corresponding K_e value) indicates near equilibrium condition. Afterwards, mineral assembly is selected based on the SI values and geochemical speciation simulation is executed. The Davies equation was used to calculate the ion activity coefficients.

Studies have reported that the adsorption of Al, Si, Ca and Mg by organic matter interaction/complexation in cementitious systems is minute [15,16,23]. This is also confirmed by our separate model trials. According to Engelsen et al. [20], the binding effects of hydrous ferric oxide (HFO) on Al, Si, Ca and Mg are very slight. Thus, the contributions from particular organic matter (POM), dissolved organic carbon (DOC) and HFO were not taken into consideration in the modelling of major elements.

The pE value ($-\log$ (electron activity)), calculated according to Eq. (2) was used to relate the oxidation-reduction condition with the leaching results and geochemical modelling.

$$pE = \frac{F}{2.303RT} E_H \quad (2)$$

pE	$-\log$ (electron activity) or the redox of the aqueous system
F	Faraday constant, 96,485.33289 C/mol
R	ideal gas law constant, 8.3144598 J/(mol·K)
T	temperature in K
E_H	measured potential in V

In the modelling, $\text{pH} + \text{pE} = 16$ was used for both systems (detailed explanation is given in section 3.2).

3. Results and discussion

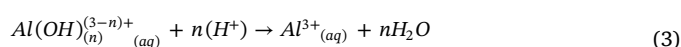
3.1. Acid neutralization capacity

Fig. 2 shows the titration curve and calculated buffer capacity of FAG and MKG mortar suspensions. It can be seen that the natural pH of FAG mortar suspension is 12.15, which is slightly higher than MKG. The pH value of suspension is affected by many factors, composition of solid precursor, dosage of alkaline activator, reaction extend of geopolymer, property of reaction product, etc. Though more activator was used during the synthesis of MKG, the reaction extent is also much higher than FAG of the same curing period [26]. The unreacted mobile alkali might contribute to the slightly higher pH value of FAG mortar suspension.

During acid addition, the pH values of both suspensions drop precipitously and then decrease modestly. This is divided into three stages for dissuasion, (I) from natural pH to $\text{pH} = 4$; (II) in the pH range of 4–2; (III) below $\text{pH} = 2$. In the first stage, the close to linear decrease might be caused by the neutralization of free alkali, rather to the dilution of the suspensions through the addition of acid. Differences between FAG mortar suspension and the MKG can also be seen within this region, this can be caused by carbonation of FAG. Slight natural carbonation is unavoidable during sample aging and pre-treatment. Benefiting from the sealed curing condition and short age, the carbonation extent is minute [26].

Further addition of acid brings a modest decrease of the pH. It can be inferred that the acid consumption in stage (II) is over twice of stage (I), while the reduced pH value is ca. 1/4 of stage (I). In addition, the MKG mortar suspension showed lower pH decrease rate than its FAG counterpart. To better interpret this region, the buffer capacity was introduced. The buffer capacity, first used by van Slyke [27], has been widely adopted to quantitatively analyse the resistance to pH change upon the addition of H^+ or OH^- ions. As shown in Fig. 2(b), a hump can be found in both FAG and MKG mortar suspensions within pH 2–4, indicating the buffer region of both suspensions.

Due to the highly complex property of the suspension, many reactions are reasonable for this buffer region in theory. One of the possible reactions is the dissolution of aluminium hydrolysis species (Eq. (3)). A similar titration plateau has been reported in [31].



The lower decrease rate in Fig. 2(a) together with the broader and

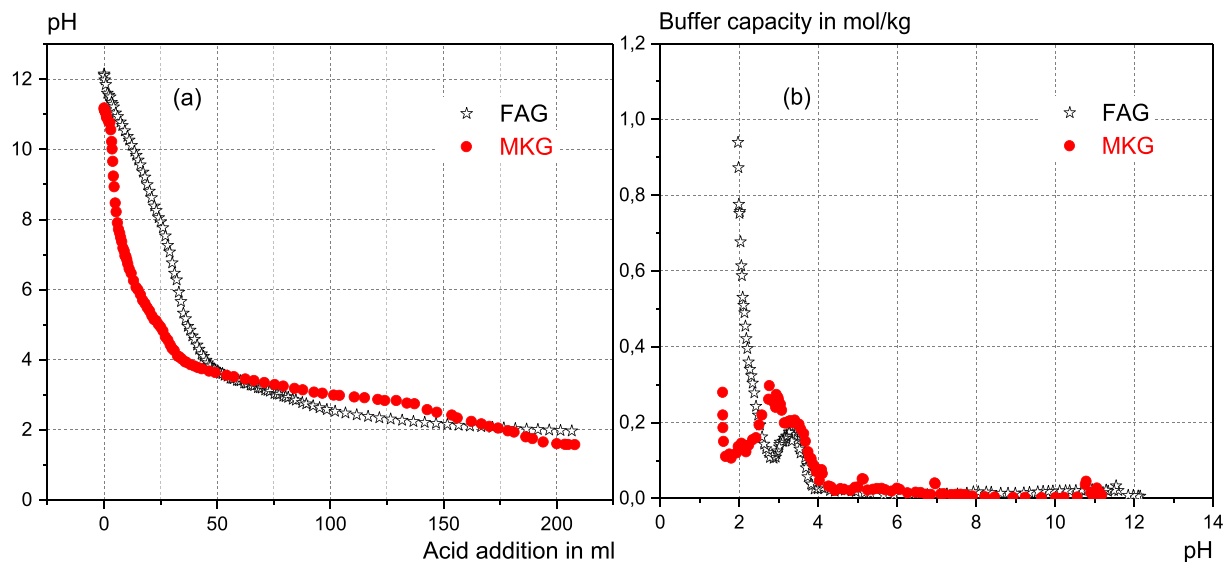


Fig. 2. Titration curves and calculated buffer capacity of FAG and MKG mortar suspensions.

higher hump in Fig. 2(b), demonstrate that the MKG mortar suspension possesses higher acid neutralization capacity in this region. The higher reactive Al content in MKG might contribute to this.

In stage (III), further addition of acid after the buffer region possesses insignificant influence on the pH value of suspension. The pH value of suspension remains almost unchanged, this phenomenon is also reflected as the sharp increase of buffer capacity within narrow pH value range in Fig. 2(b). This region is named as pseudo-buffer region, in which the solution/suspension is resisting a change of pH [27]. The resistance is not due to equilibrium buffer action, but due to the logarithmic definition of pH. Addition of some amounts of acid makes little difference on the pH because the H^+ concentration is already very high.

It should be pointed out that acid neutralization (buffer) behaviour of geopolymer mortar suspension is influenced by many parameters, such as dilution ratio and reaction degree of geopolymer, carbonation extent, etc. The titration results discussed above are preliminary. And a study of the stoichiometric mix on the buffer capacity is helpful in understanding the chemical resistance of geopolymeric gels

3.2. Eluate conductivity and pE values

Fig. 3 shows the changes of eluate conductivity with pH. The eluate

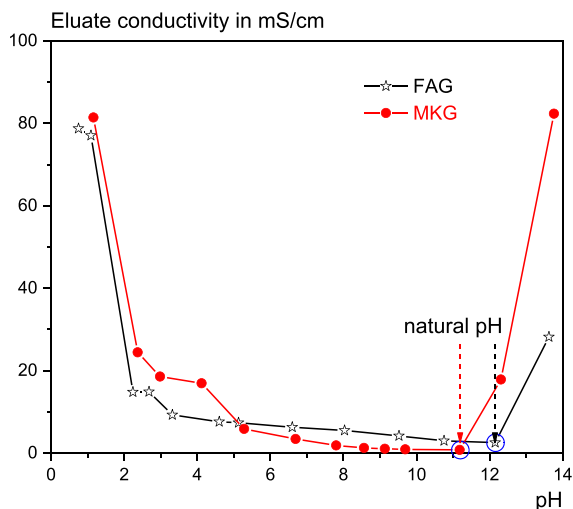


Fig. 3. Eluate conductivity of FAG and MKG mortar suspensions.

conductivity is recommended as an indicator of the total ionic strength [16,32]. For both geopolymer mortar suspensions, the conductivity increases with the decrease of pH value starting from natural pH point, indicating increased dissolution extent of solid materials. The conductivity arise in regions above natural pH can be assigned to the dissolution of geopolymers and/or unreacted solid precursors at high alkaline conditions. Moreover, the ions introduced by the addition of NaOH into the alkaline suspension also contribute to the increase of conductivity.

According to [16], the redox potential is one of the factors that influence the liquid-solid partitioning of the studied elements. The redox potential is the combined result of oxygen supply and presence of reducing/oxidising components. In this work, all vessels were sealed during leaching. Fig. 4 shows the pE values calculated based on the measured redox potential after pH dependent leaching. All the pE values are ≥ 2 , showing an oxidative environment during leaching. Within the studied pH range, the pE values of both suspensions decrease with the increase of pH value. Though not shown in Fig. 4, good linear regression results ($R^2 > 0.9$) can be obtained for both systems. And the value of (pH + pE) is approx. 16 for every measured point. Thus, pH + pE = 16 is used for the geochemical modelling.

3.3. pH dependent release of major elements

3.3.1. Leaching of chloride and sulfate

Fig. 5 shows the leaching results of chloride and sulfate from FAG and MKG. The concentrations of chloride and sulfate (as well as the other studied elements) in blank tests are around method detection limit, demonstrating no analytic interferences were introduced throughout the experiments. Both components exhibit virtually pH independent leaching behaviour with the concentrations remaining relatively constant within the studied pH range. According to Kosson et al. [16], components with this phenomenon can be regarded as availability-limited leaching. The availability is not referred to the bulk amount initially contained by source materials, but to the fraction that is not bound in recalcitrant phases. In the pH leaching, the available content is defined as the highest leached quantity [16]. Compared with the bulk content in solid precursors, the available content can better reflect the leaching property of studied elements. In this work, 70–80% of chloride and sulfate are leached from FAG and MKG, indicating that both components are mainly present in readily soluble species.

The pH independent leaching results of chloride have been underlined in several studies, including cementitious materials, incinerator

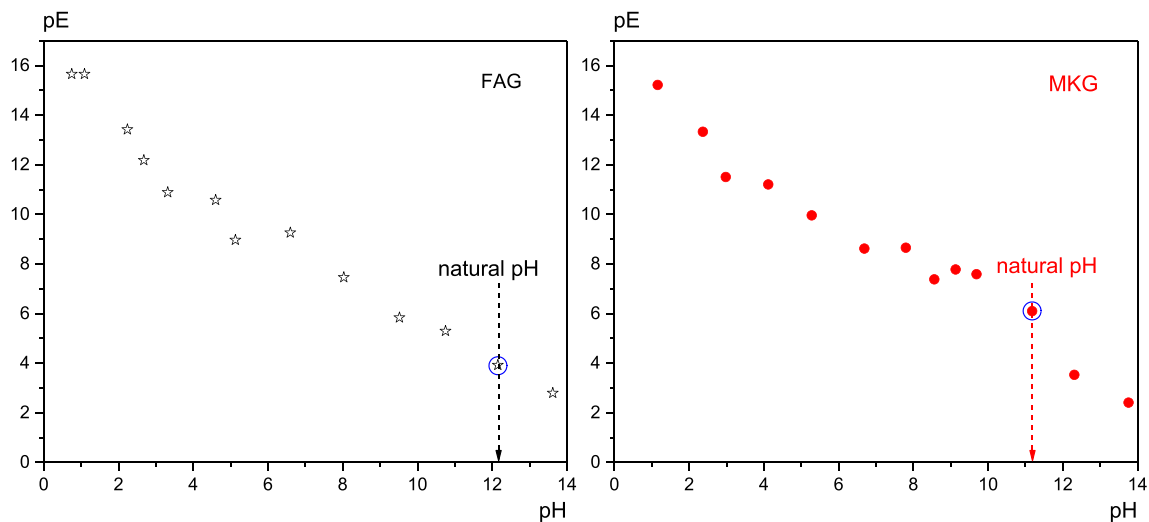


Fig. 4. pE values of FAG and MKG mortar suspensions.

ashes, inorganic landfills, etc. [16,33]. In contrast, the leaching of sulfate varies from study to study. Precipitation of ettringite in cementitious system results in decreased leaching of sulfate at $\text{pH} > 10$ [16,20]. The degradation of AFt and AFm phases in aged concrete can increase the available content of sulfate [20]. All these processes can be excluded in this work, due to the low calcium content of FAG and MKG.

3.3.2. Leaching of K and Na

The leaching behaviours of K and Na are shown in Fig. 6. Both elements show pH dependent leaching characteristics. The minimum release of K was obtained at material's natural pH, higher and lower pH values result in increased leaching of K from both geopolymers. A similar trend can be seen in terms of the leaching of Na from both geopolymers, but it should be mentioned that NaOH solution was added in suspensions of higher pH values than natural pH. In these suspensions, the measured amount of Na in eluate is less than the quantity added via NaOH. All these indicate that the added NaOH takes part in the reactions during leaching process, and is present in less soluble phases.

For comparison leaching results of K and Na from CEM I mortars [17] are also shown in Fig. 6. Kosson et al. [16] stated that the leaching of periodic table Group IA elements is not strongly influenced by pH, which is also verified by other researchers [18,34,35]. A close check of the materials used in these studies shows that the Na and K are mainly present as chloride salts. In [36], the leaching of K and Na from aged fly

ash showed pH dependent characteristics, while from fresh fly ash not. In this work, a significant fraction of K and Na are bound to aluminosilicates. Substitution of silicon by aluminium has been detected in many aluminosilicate minerals and in the geopolymeric gel framework [4,6,37,38]. The associated negative charge is balanced by alkali cations [6]. Perrott [39] investigated the surface charge characteristics of amorphous aluminosilicates in pH range of 4–9. Results showed that amorphous aluminosilicates possess pH dependent surface charges, and the negative charges increase with pH.

Differences in terms of the leaching behaviour between K and Na can be inferred from Fig. 6. Much higher concentrations of Na than K were detected in both geopolymers. This is caused by the excess mobile Na from the activator. In contrast, K originates from solid precursors where it is mainly present in amorphous phases. As reported by Duxson et al. [40], K is preferentially incorporated into the gel phase. But dissolved potassium has been detected in pore solutions of different geopolymers synthesized using K-free activator [41,42]. This part of potassium can be easily leached out at neutral pH values. The leaching of K from both geopolymer shows similar trends and the results are close to parallel especially in the range below natural pH, while the leaching of Na differs. This indicates that K and Na may exist in different forms in geopolymer. In many aluminosilicate phases, such as montmorillonite, Na^+ has the tendency to form inner surface complexes with tetrahedral charge sites [39,43]. K^+ is less dependent than

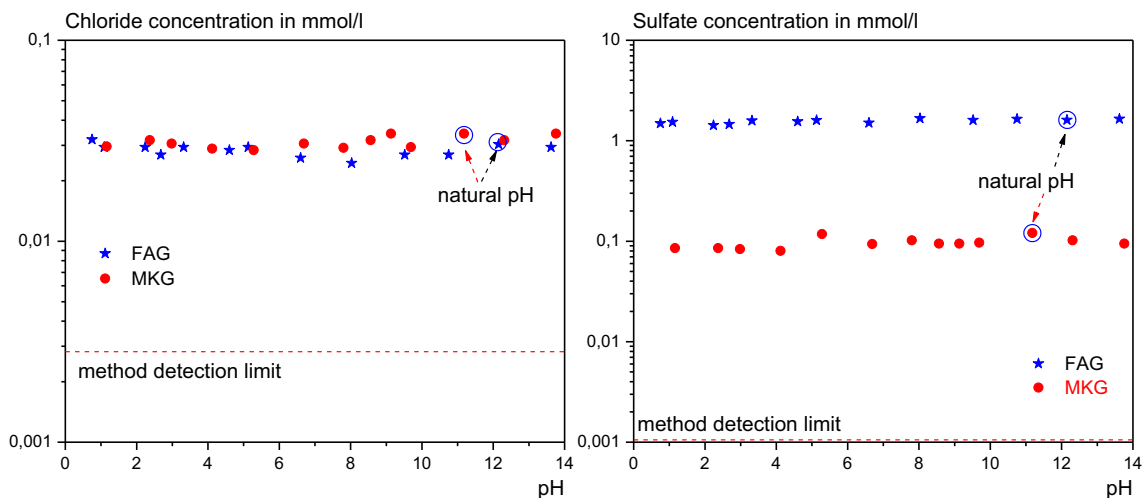


Fig. 5. pH dependent leaching of chloride and sulfate from FAG and MKG mortars.

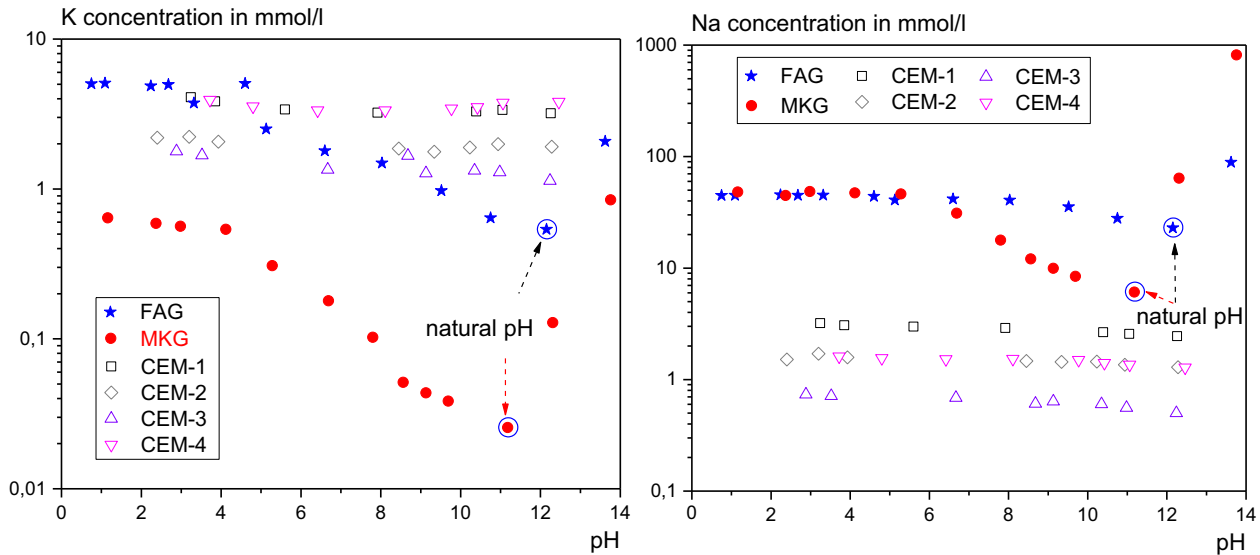


Fig. 6. pH dependent leaching of Na and K from FAG and MKG mortars (cement data from [17], CEM-1, CEM-2, CEM-3 and CEM-4 are designated as H1, N1, H3 and D1 in [17], respectively).

Na^+ on the location of the charge site because the facile de-solvation property and large radius [39,44].

3.3.3. Leaching of Si and Al

Fig. 7 shows the leaching results of Si and Al from both geopolymers. Both elements showed amphoteric leaching behaviour, where the concentration increases at acidic and alkaline conditions. For Si, the minimum leaching takes place around pH 10 for both geopolymers. Higher or lower pH values contribute to the release of Si from the solid to the aqueous solution. In addition, the leached amount of Si from MKG is higher than from FAG in acidic condition, especially when $\text{pH} < 4$. This might be caused by many factors, including the higher mobile Si dosage from activator of MKG, more Si-bearing crystalline phases in FA, etc. While in basic condition, leached amounts of Si from both geopolymers are similar, regardless of the initial higher Si content in MKG system. In comparison with the leaching of Si and Al from OPC mortar, differences can be seen at $\text{pH} > 10$. This might be caused by the difference of cement and geopolymer in chemistry, which deserves further investigation.

Both geopolymers show high and close to stable Al concentration in

$\text{pH} < 4$. The lowest aluminium concentrations occur at pH around 5. The significant decrease of Al concentration might be caused by the formation of aluminium hydroxide. In alkaline conditions, the Al concentration then increases with the increase of pH value.

It can be inferred from Fig. 7 that pH has significant influence on leaching preference of Si and Al from both geopolymers. Si and Al are predominant framework components of alkali aluminosilicate-type gel (N-A-S(H)), which is the main reaction product of geopolymers. The release properties of Si and Al are essential in understanding the chemistry of N-A-S(H) gel. Fig. 8 plots the molar ratio of leached Al-to-Si, which is the steady-state dissolution result of both geopolymers. As aforementioned, formation of $\text{Al}(\text{OH})_3$ takes place mainly around pH 4–8, resulting in the low content of Al in eluate. Thus the significant scatter of Al/Si ratio in this region is excluded from the following discussion.

As shown in Fig. 8, the eluate Al/Si ratios of FAG system in acidic and basic conditions are significantly different. Meanwhile, close to constant Al/Si ratio is obtained by the MKG in $\text{pH} < 4$ and $\text{pH} > 8$. This raises curiosity about the dissolution property of different geopolymer binders, which can be influenced by the physicochemical

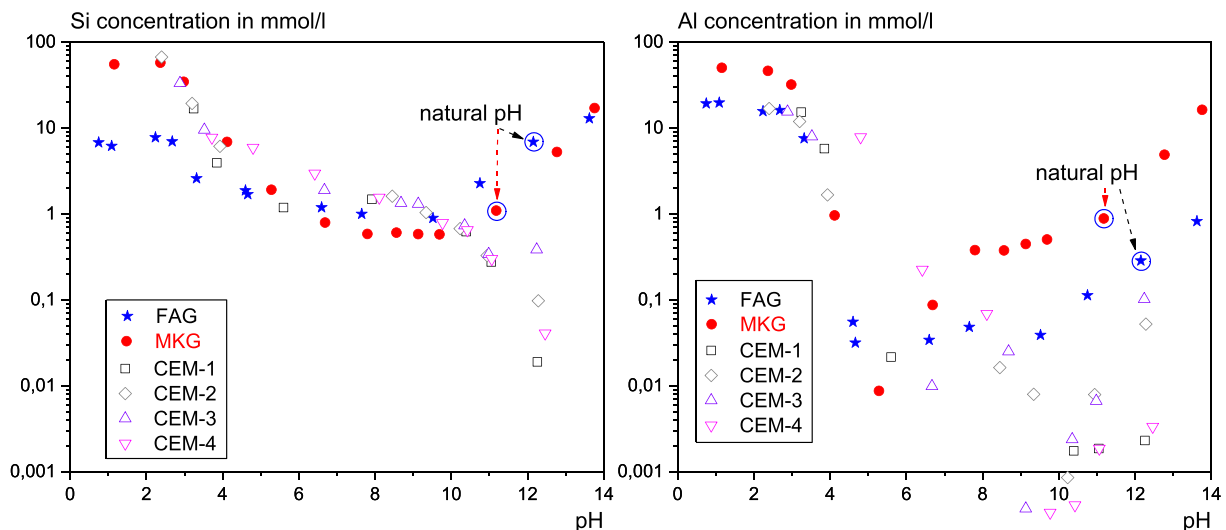


Fig. 7. pH dependent leaching of Si and Al from FAG and MKG mortars (cement data from [17]).

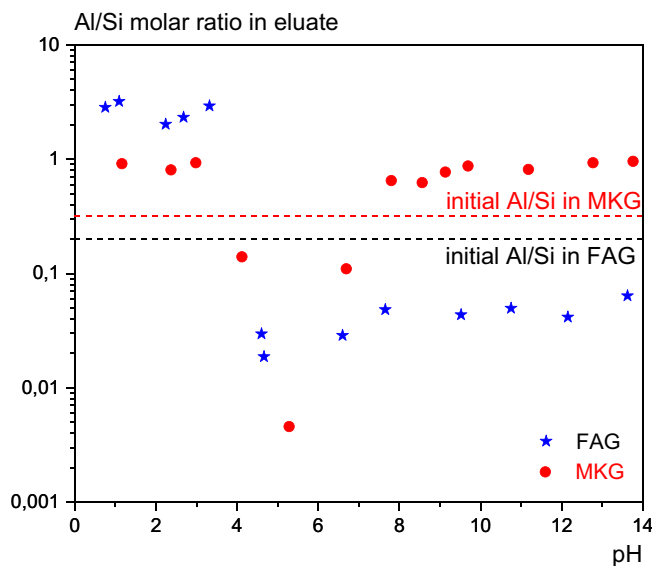


Fig. 8. Molar ratio of leached Si and Al from FAG and MKG at different pH values.

properties of source materials, mix design, reaction degree, etc. A study about the effect of stoichiometry on dissolution property of geopolymeric gel is also needed to better understand the chemistry and stability of geopolymer.

The higher Al/Si-ratio compared to the initial ratio might be caused by the preferential release of Al from both geopolymers in acidic condition and/or precipitation of dissolved Si (see section 3.5). In pH > 8, precipitation of Al and Si will be gradually inhibited. At high pH a lower than initial Al/Si is obtained by the FAG, which demonstrates that Si appears to be more preferentially released than Al from FAG in basic condition. In contrast, the MKG system behaves counter to this.

Incongruent dissolution of (alumino)silicate structures has been widely recognised and found to be pH dependent. Extensive studies have been conducted using natural or artificial synthesized minerals in the past decades [43,45,46]. Recently, different models have been developed to reveal the dissolution process of minerals in acidic and alkaline conditions [47,48]. Though the mechanism of dissolution of (alumino)silicate minerals has not been described in satisfactory manner, studies have demonstrated that the partially preference release of Si and Al can result in the disintegration of the aluminosilicate structures. In this case, MKG synthesized in this work seems to possess higher stability under acidic and basic attack than FAG, because of the more significant deviation of leached Al/Si from initial ratio of FAG.

3.3.4. Leaching of Ca and Mg

Ca and Mg are the typical alkaline earth metals contained by solid precursors. Fig. 9 shows the leaching results of both elements.

As shown in Fig. 9 and reported in patterns [16,19,49], the pH leaching of Ca and Mg from cement concrete and incinerator ashes show cationic patterns, in which high leaching concentration is maintained in extreme acidic condition and decreases as the pH increases.

In this work, leaching of Ca and Mg from both geopolymers are orders of magnitude lower than for CEM I mortars. The highest concentrations were achieved in acidic condition. The leaching behaviour of Mg is consistent with cationic pattern. In contrast, the leaching of Ca showed amphoteric characteristic, with the lowest concentration taking place at natural pH. Increased dissolution of Ca was obtained in both higher and lower pH values. This phenomenon differs from many of the reported pH leaching studies in terms of cement-based materials [16,20,50], indicating different existence state of Ca between geopolymer and cement concrete. This will be further discussed in Section 3.6.

3.4. Leaching results of minor and trace elements

Apart from the major elements discussed above, the leaching of minor and trace elements is also studied. The leaching of minor and trace elements also show strong dependence to suspension pH. In this work, the 15 elements measured are divided into the following two groups to show the leaching characteristics with some representative elements.

3.4.1. Leaching of metal cations

Fig. 10 shows the leaching results of Sr, Zn, Co and Cu. The leached amounts for all these elements are at their maxima in the extreme acidic region, pH < 2. The overall leaching of Zn and Sr are found to be of cationic pattern. Though not shown here, the leaching of Pb, Mn and Sb from geopolymers also show a similar trend. The low solubility of potential phases incorporating these elements in alkaline condition is assigned as one of the main controlling factors [19]. Such elements are generally well immobilized in intact geopolymer paste [2,14].

In contrast, a tendency towards an amphoteric leaching behaviour was obtained for Cu and Co shown in Fig. 10. Leaching of Ni from geopolymer is similar. According to Engelman et al. [19], HFO and DOC play significant role in the pH leaching of Cu and Ni from cement concrete. This provides reference for figuring out the solubility controlling phases of these elements in the future. The concentration increase in strong alkaline condition indicates the decomposition and/or transformation of the solubility controlling phases [19].

3.4.2. Leaching of oxyanionic ingredients

Fig. 11 shows the leaching results of As and V. Both elements show a leaching style different from all the patterns mentioned above. In addition to the maximum leaching concentration in the most acidic condition, another concentration peak was obtained at material natural pH with the minima at pH 4–6. Concentration decrease can be observed when pH is higher than natural pH. In principle, the difference is due to the negative charge of the oxyanions [49,51]. The chemical bonding between oxygen and metal is covalent in the oxyanions. In this work, analogue transition for Mo, Cr and Se were found. Several studies have pointed out the oxyanionic pattern in terms of the leaching of these elements from cement concrete, fly ash and soil [19,49]. The destabilisation of hydrate phases at pH higher or lower than natural pH is reported to be responsible for the concentration decrease in cement concrete system [19]. In addition, the HFO is rather crucial in the leaching of oxyanionic ingredients in many systems [16,19]. The role of HFO on leaching of these elements from geopolymer will be covered by further investigations. Unlike the abovementioned elements, the detected concentration of As and V are higher than for cement mortars, especially in alkaline conditions. This should be further investigated to ensure the environmental compatibility of geopolymers.

3.5. Mineral phase evolution

After the leaching test, the solid residues were collected and measured using XRD to reveal the dissolution/precipitation characteristics of the geopolymer mortars at different pH values. Results are shown in Fig. 12. The sample ID is the combination of solid type and pH value. For instance, FAG and MKG-1.16 represent FAG before leaching and MKG after leaching at pH value of 1.16.

New reflections at 6.3°, 19.8° and 36.0° 2θ were detected in both geopolymers after leaching, which can be attributed to the formation of montmorillonite ((Ca,Na)_{0.3}Al₂(Si,Al)₄O₁₀(OH)₂nH₂O, PDF No. 00-060-0318). Montmorillonite, a member of the smectite group, has a sandwiching structure of two tetrahedral sheets of silica with an octahedral sheet of alumina in the middle [52,53]. The tetrahedral sites can partially be substituted by alumina. The negative charges caused by the unbalanced substitution are neutralized by Na⁺ or Ca²⁺, which are normally located in the inter-lamellar space [53]. Montmorillonite clay

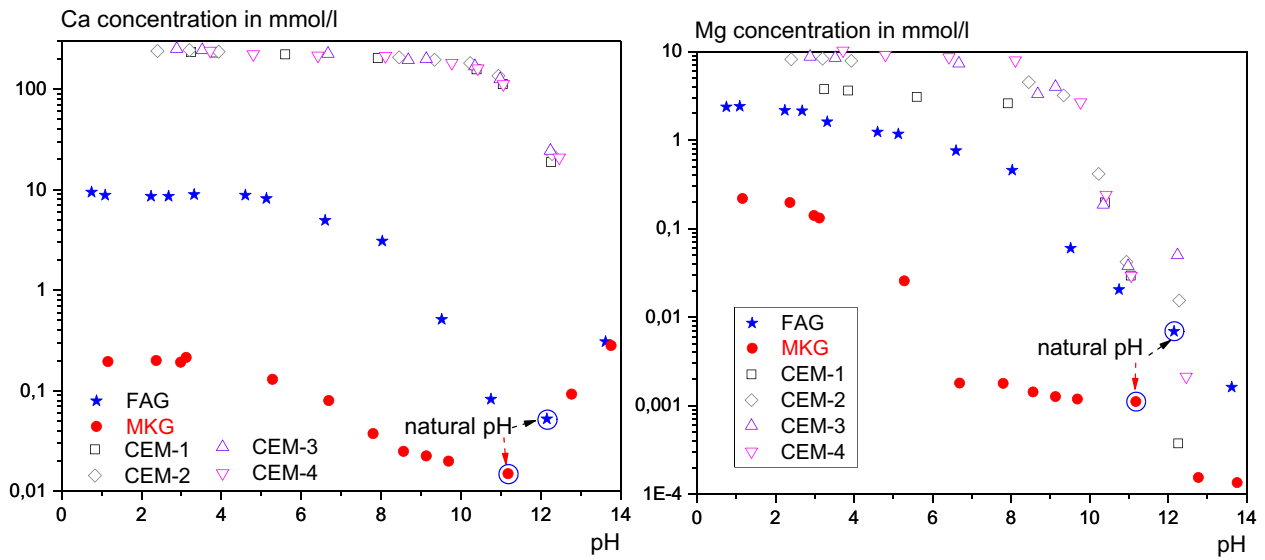


Fig. 9. pH dependent leaching of Ca and Mg from FAG and MKG mortars (cement data from [17]).

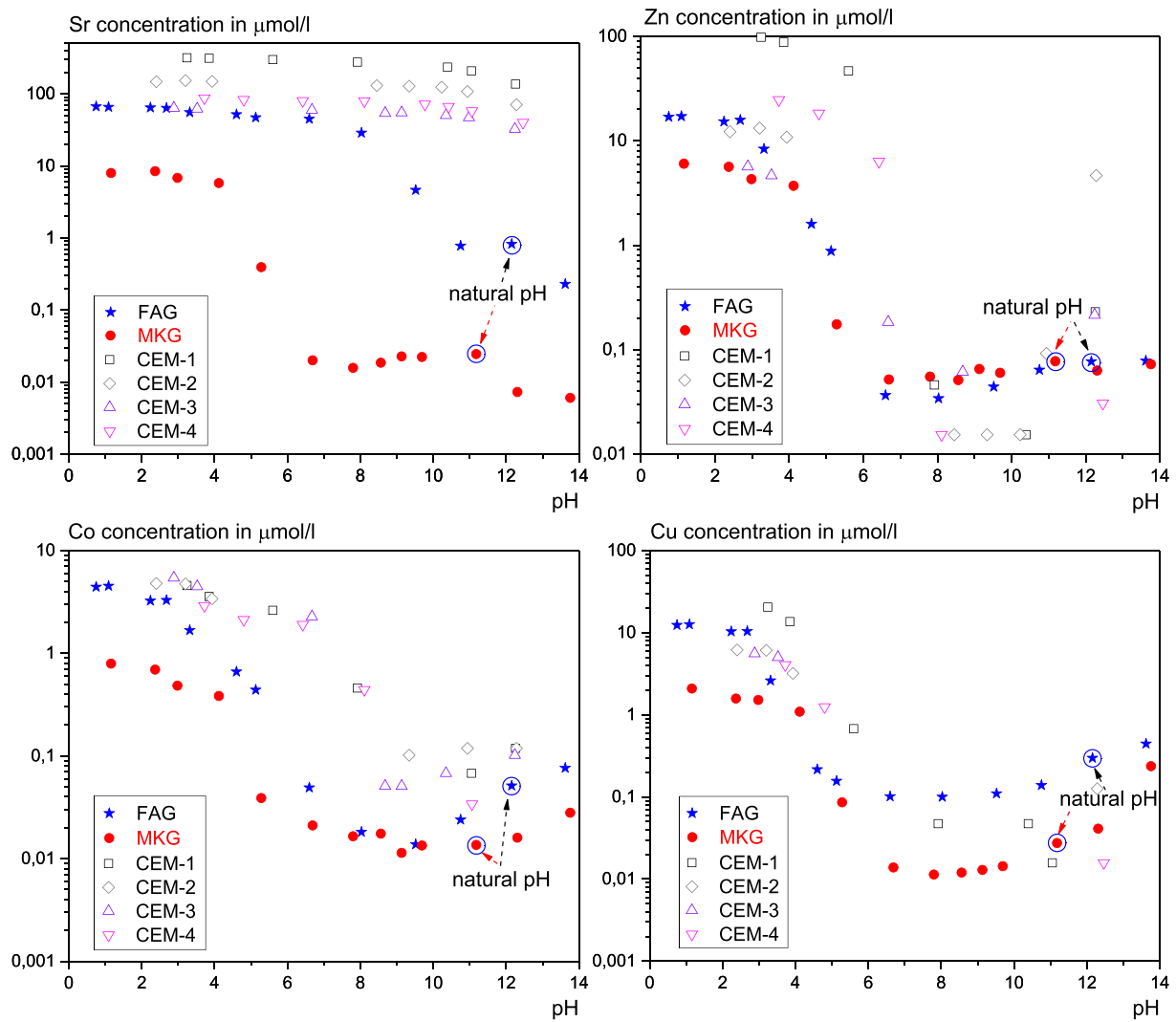


Fig. 10. pH dependent leaching of Sr, Zn, Co and Cu from FAG and MKG mortars (cement data from [17]).

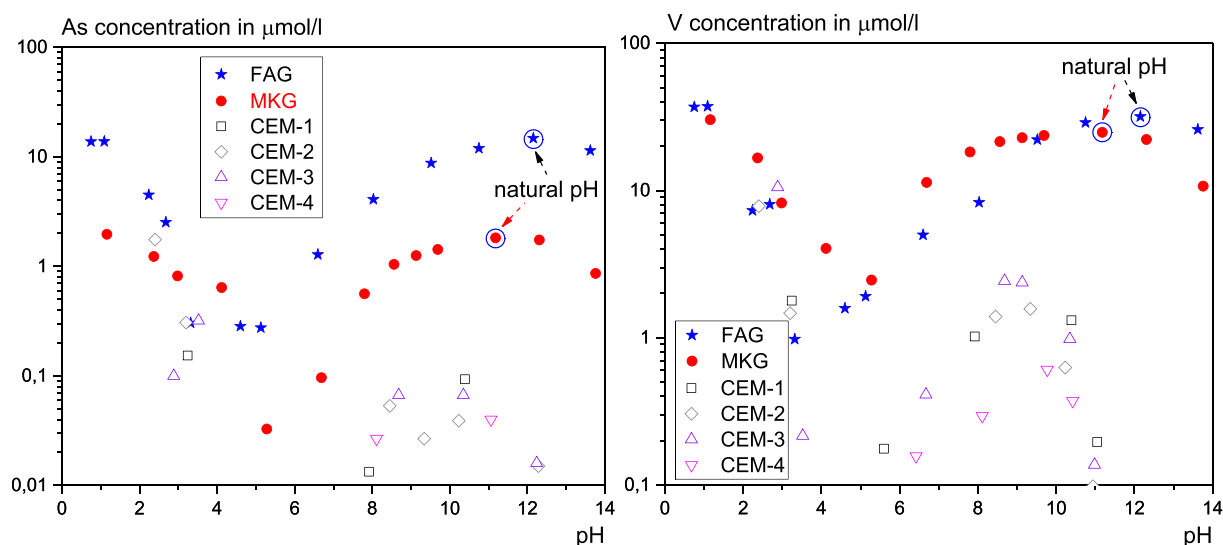


Fig. 11. pH dependent leaching of As and V from FAG and MKG mortars (cement data from [17]).

has been extensively studied since its broad range of applications. Different routes have been developed for the synthesis of montmorillonite, using hydrothermal technique from moderate to extreme conditions with different precursors [52]. Meanwhile, montmorillonite with not well crystallized structure has been synthesized by Harder, Tomita and other researchers [52,54,55] at ambient condition. The leaching condition of this work meets the broad synthesis conditions reviewed in [52].

Apart from the formation of montmorillonite, the amorphous hump centring around $15\text{--}35^\circ 2\theta$ increased after leaching at pH values below natural pH (see Fig. 13). As shown above, the dissolution of studied elements at pH above natural pH is similar with or even higher than those in extreme acidic conditions. But insignificant differences can be found from XRD patterns of these samples in $15\text{--}35^\circ 2\theta$. It can then be inferred that the intensity increase of the amorphous hump is caused by the formation of new amorphous or microcrystalline phases. The newly formed phase can be assigned to amorphous silica. Amorphous silica was used by Engelsen et al. [20] in the geochemical modelling of the pH leaching results of cement concrete, though no evidence about the formation of amorphous silica has been given.

The precipitation mechanism of amorphous silica in aqueous solution has been extensively studied both by experiment and simulation [56–60]. The whole process can be simplified as formation of primary particles and subsequent flocculation/condensation. Formation and thermodynamics of silica nanoparticles in mildly neutral to basic conditions have been investigated in [58,59,61,62]. Gorrepati et al. [57] revealed the precipitation of silica during the dissolution of aluminosilicate zeolite in acidic conditions. The Si dissolved from analcime in acid behaves identically to adding acid into concentrated monosilicic solutions. The precipitation can be exponentially enhanced by increasing acid concentration. In addition, the co-existence of other ions, such as Al^{3+} , Ca^{2+} , Na^+ , Cl^- , etc., contributes to accelerate the rate of particle formation and growth.

The main reaction product of geopolymer is amorphous N-A-S-(H) gels, which normally locate around $25\text{--}30^\circ 2\theta$. In comparison with unleached samples, not much difference can be seen within this region no matter in acid or alkaline conditions. This demonstrates the high stability of geopolymer under chemical attack.

3.6. Geochemical modelling of Al, Si, Ca and Mg

The pH leaching experiments discussed above reveal the partitioning characteristics of studied species between solid and aqueous

phase at different pH values. Geochemical modelling has been demonstrated to be powerful in exploring the leaching mechanism and figuring out potential solubility controlling phases [19,20]. In this work, pilot-scale practices are made on the geochemical modelling of Al, Si, Ca and Mg from geopolymers.

Mineral phases were determined from the XRD measurement. Phases, such as $\text{C}_4\text{A}\bar{\text{C}}_{0.5}\text{H}_{11.5}$, $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$, C_4AH_{13} , Wairakite, C_3FH_6 , $\text{C}_4\text{F}\bar{\text{S}}\text{H}_{12}$, etc., frequently used by researchers in the geochemical modelling of cement are also considered in this work. Many of these phases are excluded based on the saturation indices and separate model trials (not shown here). The main reaction product of FAG and MKG is the N-A-S-(H) gel. Meanwhile, thermodynamic property of this phase is still not fully known and studies are ongoing [63,64]. To fulfil the gap caused by lacking thermodynamic data of N-A-S-(H), the recently updated thermodynamic data of C-(N)-A-S-H solid solution (CNASH_{ss} in abbreviation) were incorporated into the OCESTRA. Formation of calcium modified N-A-S-(H) gel ((N,C)-A-S-(H)) is plausible in principle in the geopolymers synthesized in this work [26]. Using CNASH_{ss} may increase the uncertainty of the modelling, nevertheless it provides a way to compare the differences of gels and to collect feedbacks for further improvement.

Though challenging, the modelling work was conducted mainly without any fitting of the parameters. The considered elements were modelled simultaneously with one set of minerals and solid solutions. The modelling results of FAG are shown in Fig. 14 for discussion. According to Engelman et al. [19,20], a difference of less than half an order of magnitude between the measured and simulated leached concentrations is considered as an adequate match. In contrast, a fair modelling result represents an overall agreement varied for over two orders of magnitude over the pH range.

In the modelling of Al, a fair correlation between predicted and measured concentrations is given, especially in the pH range of 4–9. Apart from the uncertainty caused by CNASH_{ss}, the ideal phase parameter used as input might be responsible. The fact that the equilibrium concentrations changed several orders of magnitude challenges the modelling. In addition, the solubility of precipitated $\text{Al}(\text{OH})_3(\text{am})$ decreases with time, and values provided by different databases vary ($\log(K_e) = -13.57, -10.38, -9.242$ in Cemdata 18, MINTEQ and ECN, respectively). It can still be inferred from the modelling result that precipitation of $\text{Al}(\text{OH})_3(\text{am})$ is the main controlling factor in pH = 4–9, which confirms the above assertion. In extreme acidic condition, Al not bound in recalcitrant phases is preferentially dissolved. The concentration predicted by the model is in adequate agreement

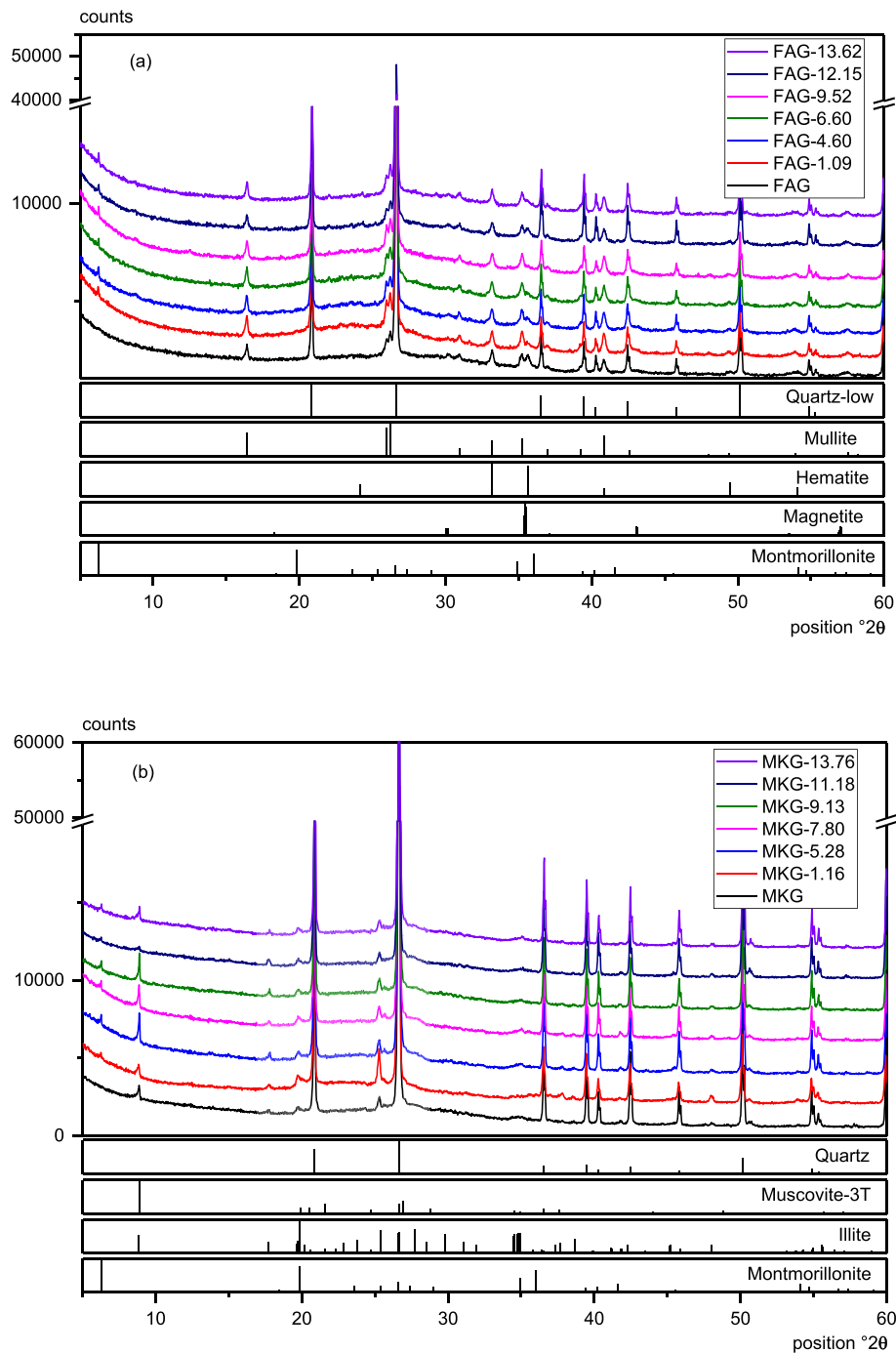


Fig. 12. XRD patterns of FAG and MKG samples before and after leaching tests.

with the measured concentration in this region. In alkaline conditions, M_4AcH_9 and CNASH_{ss} are the main controlling phases. The M_4AcH_9 is hydrotalcite-like layered double hydroxide (LDH), which sometimes is abbreviated as $MgAl-CO_3-LDH$. Formation of M_4AcH_9 is typical in cementitious system [63]. The amount of M_4AcH_9 might be minute since no reflection peaks were determined in XRD measurement. Similar assertions can be made for the formation of natrolite and calcite (in the modelling of Ca). As predicted by the model, zeolite phase natrolite is also a retention phase. Formation of natrolite has been reported in cementitious system. The thermodynamic model and solubility data of natrolite were well investigated by Lothenbach et al. [30,65]. Zeolite phases are also frequently determined in geopolymeric system due to the similarity between geopolymerization and zeolite formation. In

[20,37], zeolite phase was also reported as one of the controlling phases in the release of Al and Si from cement concrete.

The model showed better agreement between predicted and experimental concentrations of Si than of Al. The CNASH_{ss} mainly influences the leaching of Si in alkaline condition. Though the CNASH_{ss} was recommended for the alkali activated systems, the CNASH_{ss} can only well represent the solubility data of C-(N)-A-S-H gel phase with $Ca/Si \geq 0.67$ [30]. As mentioned above, formation of (N, C)-A-S-H gel is plausible in principle, but the Ca/Si in both FAG and MKG is lower than 0.67. In acidic condition, amorphous silica is found as the solubility controlling phases. The Si concentration was overestimated in the pH region 3–10, when natrolite was not used as the solubility controlling mineral in separate model trials. The retention effects of Si shown in

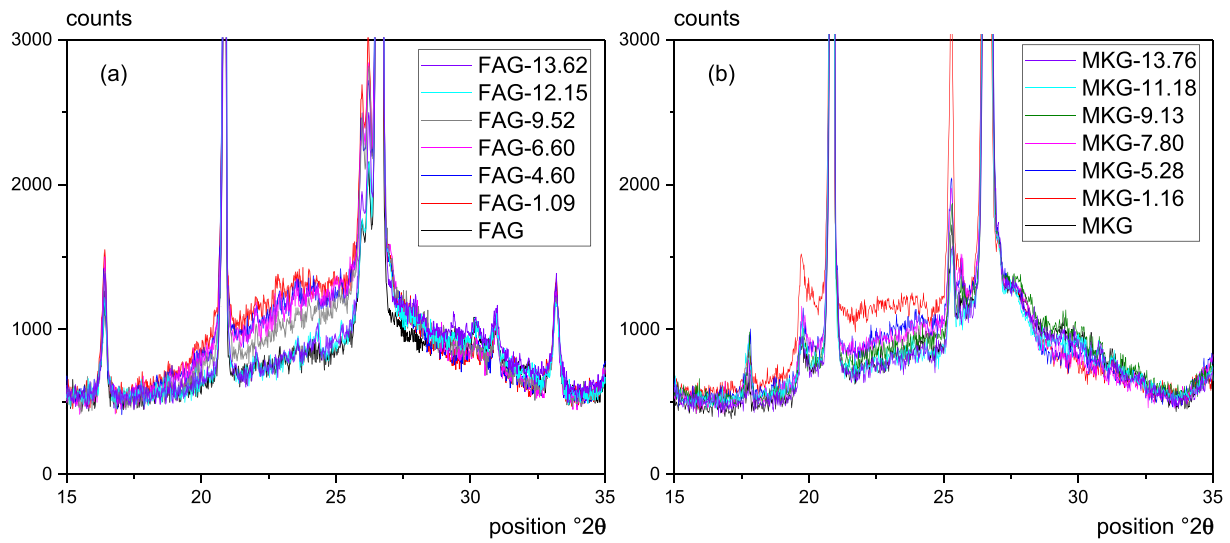


Fig. 13. Section of 15–35° 2θ of the XRD patterns of FAG and MKG samples before and after leaching tests.

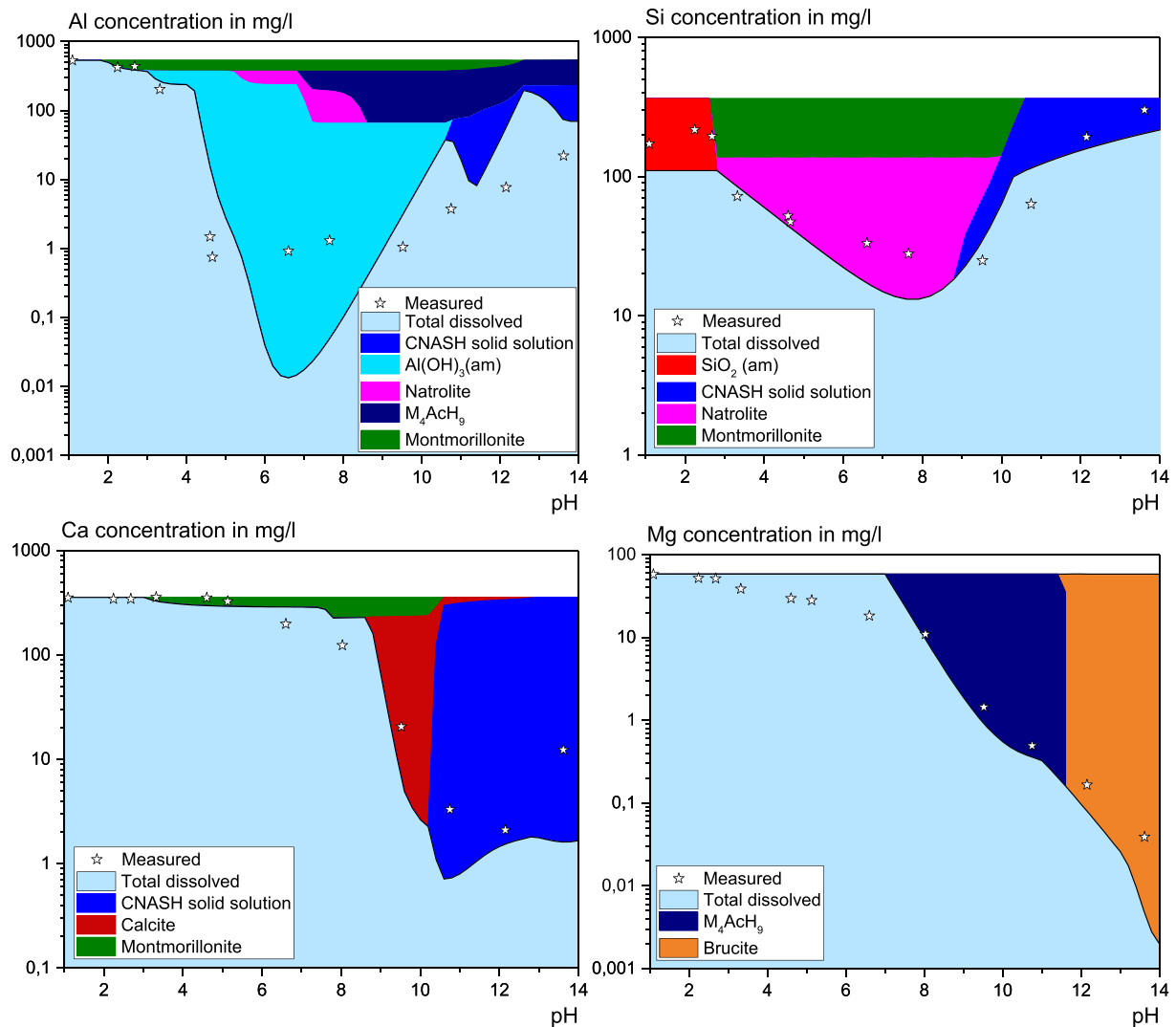


Fig. 14. Experimental (leached) and predicted (geochemical modelling) concentrations of Al, Si, Ca and Mg in the eluates from FAG mortar as a function of pH.

Fig. 14 are more likely a mixture of other aluminosilicate phases that have similar thermodynamic characteristics with natrolite. It should be noted that the leached K and Na concentrations also vary in this region, which supports the K and Na containing minerals in principle. Further investigation of the corresponding minerals is necessary.

Compared with the retention effect on Al and Si, the CNASH_{ss} possess more significant influence in the leaching of Ca. The role of Ca during geopolymerization is not fully clear [37,38,66,67]. In alkali activated materials with medium calcium content, coexistence of C-A-S-H and N-A-S(H) has been detected in alkali activated materials with medium calcium content [68]. ((N,C)-A-S-H) was observed in AAM of calcium-poor formulation. The FAG meets the formation condition of this (N, C)-A-S-H gel. The feasibility of CNASH in geochemical modelling of Ca may confirm the existence of (N, C)-A-S-H. But this should be further investigated with other techniques.

The modelling results show that the solubility controlling phases of Mg are hydrotalcite and brucite. In cement concrete, hydrotalcite and brucite are also reported as the predominant solubility controlling phase [20]. The initial content of MgO has been reported has influence on the mechanical property and durability of AAM [69,70]. Bernal et al. [71] has demonstrated the MgO content mainly influences the formation of secondary product rather than the (sodium)-calcium-aluminosilicate gels.

Isomorphous substitutions of Mg for Al in the central alumina plane of montmorillonite normally take place, especially in ambient synthesized montmorillonite [52]. And according to Klopogge et al. [52], Mg-bearing components are frequently used as precursor for the synthesis of montmorillonite at ambient conditions. Whether the formed montmorillonite contains Mg and has an influence on the leaching of Mg deserves further investigation.

The modelling of Al, Si, Ca and Mg from MKG was also conducted, but results were not better than the FAG system shown above. The higher Si/Al ratio and lower calcium content in MKG further curtails the suitability of using CNASH_{ss} in geochemical modelling. Hence, the influence of stoichiometry on the physicochemical properties of geopolymeric gel is of great concern. Further improvements will be made when the corresponding database is available. Geochemical modelling of the heavy metals and trace elements from geopolymers will be covered in our following work.

The geochemical modelling offers a detailed insight into the contributions from specific species and the assemblages of solubility controlling phases. Though uncertainties and unsolved questions exist in the geochemical modelling, these uncertainties and questions are essential feedbacks for further investigation of the chemistry of alkali activated materials.

4. Summary and conclusion

In this work, the pH dependent leaching characteristics of major and trace elements from FAG and MKG mortars were studied. Mineral evolution before and after leaching was characterized, which was used for the geochemical modelling to identify the solubility controlling phases of Al, Si, Ca and Mg. This work is not only fundamental for environmental compatibility assessment of geopolymers, but also offers insight to deepen the understanding of geopolymer in chemistry.

Both geopolymers showed similar acid neutralization property, but the MKG possesses higher buffer capacity in acid region. The leaching results provide direct insight into the partitioning of chemical species between the solid and aqueous phase at different pH values. Leaching of chloride and sulfate showed virtually pH independent characteristic, while cationic and oxyanionic leaching patterns were detected for the others elements.

After leaching, formation of montmorillonite was detected in all samples, and amorphous silica was founded in samples with pH values below natural pH. The intensity of amorphous silica increased with the decrease of suspension pH. In comparison with un-leached samples, not

much difference can be seen within the X-ray diffraction region of N-A-S-H. Pilot-scale practices in terms of geochemical modelling were made to identify the solubility controlling phases of Al, Si, Ca and Mg. Results offers a detailed insight into the contributions from specific species and the assemblages of solubility controlling phases. Limited by the lack of thermodynamic data for geopolymeric phases, uncertainties and unsolved questions exist in the geochemical modelling. In addition, the individual SI calculations do not capture properly multi-element interactions, and the high salt load in the leaching system gives limitations with the use of Davies equation. All these should be considered for further optimization of the geochemical modelling of geopolymer.

Though XRD measurement contributes to the mineral phase detection and screening, several phases identified by XRD are not relevant from a leaching controlling perspective. Surface coating minerals formed due to the exposure of minerals to the atmosphere are normally more leaching relevant. In addition, the mineral phases of minor quantity can be of relevance for leaching in many cases. More advanced characterisations of the geopolymer before and after leaching are needed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests that could have appeared to influence the work reported in this paper.

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Leaching of monolithic geopolymer mortars

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ABSTRACT

The environmental compatibility of geopolymers was investigated in this work in terms of the leaching properties of major components, heavy metals and trace elements from monolithic mortars. Fly ash geopolymer, metakaolin geopolymer and a commercial geopolymer mortar were used. Leaching mechanism analysis demonstrates that the leaching of chemical components is mainly controlled by diffusion, while surface wash-off, solubility and depletion also take place. The results were compared with cement-based materials and the regulatory limits in Germany and in the Netherlands for environmental compatibility assessment. Leaching of studied heavy metals and trace elements (except B, V and Mo) from geopolymer are in a similar range as cementitious materials. Only the cumulative release of V is higher than the threshold in Germany, but it still meets the requirement in the Netherlands. Strength decrease after leaching was detected, which was 11.8%, 9.4% and 14.9% for fly ash geopolymer, metakaolin geopolymer and the commercial geopolymer, respectively. In addition, no difference in terms of phase composition in the surface layer was detected after leaching.

1. Introduction

Geopolymer refers to a group of low-calcium materials synthesised by alkali activation of aluminosilicates [1,2]. As a sub-class of alkali activated material (AAM), geopolymer-based materials are reported to possess properties of high mechanical strength, stability under thermal and chemical attack, strong adhesion on various surfaces, low permeability, etc., [3]. In addition, geopolymer concrete can significantly reduce CO₂ emission in comparison with ordinary Portland cement (OPC) concrete [1,3].

Geopolymer has been recognised as a potential immobilization matrix of hazardous wastes [2]. Numerous efforts have been made in solidifying/stabilising toxic species via the geopolymer technology. According to [4,5] heavy metals, such as Cd(II), Cu(II) and Pb(II) can be effectively immobilized in geopolymers. The immobilization process is complex and involves encapsulation of contaminants, physical adsorption, chemical fixation, etc. [2,6]. In the case of lead, the formation of Pb-silicate compounds with very low solubility contributes to the binding [4,5]. In addition, lead was also reported to modify the pore structure of geopolymer. An increase of immobilization efficiency with the increase of the radius of the studied components was confirmed in [7]. Some studies hypothesized that heavy metal cations like Zn(II), Cu(II), Cd(II) and Cr(III), can replace alkali cations in balancing the negative charge caused by the substitution of silicon by aluminium [8,9]. This process is excluded in [6,7] because reduced leaching of alkali ions

from geopolymer was observed after artificially incorporating heavy metals. However, only eluate conductivity was measured and used to evaluate the leaching behaviour in [6,7], which cannot be considered absolutely conclusive. El-Eswed et al. [7] also proposed the formation of coordination bonds between heavy metals ions and the non-bridging Si–O/Al–O end members. This identification was only based on the qualitative evidences from Fourier-transform infrared spectroscopy (FTIR) study and deserves in-depth investigation.

The stabilization behaviour also relies on the chemical properties of the compounds containing the toxic elements. Guo et al. [10] reported that Pb can be dispersed throughout the geopolymer matrix and chemically bound when being added in soluble form (e.g. PbO, PbSO₄). In contrast, PbS, inert to alkaline condition, was found to be segregated from the binder. Meanwhile Cr(VI) was highly leachable when added as a soluble salt (for example Na₂CrO₄) [5,11]. Converting Cr(VI) to less toxic and less mobile Cr(III) was an effective method, for which sodium sulphide (Na₂S) or ferrous compounds were adopted. Highly soluble salts are preferable for the reduction process prior to the setting of the geopolymer [11]. The abovementioned efforts contribute to promote the application of geopolymer for wastes immobilization.

Geopolymer possesses superior engineering properties of being used as construction and building materials. However, the approval for field application of geopolymer will depend not only on its mechanical properties, but also on its environmental credits in terms of the release of potentially harmful components into the surrounding environment.

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Solid precursors for geopolymer synthesis include a wide variety of industrial wastes and by-products, such as fly ash, metallurgical slags, mineral processing tails, etc. [7,8]. Moreover, these materials normally contain higher amounts of toxic chemical components than cement [12,13]. In contact with water, major components, heavy metals and trace elements from these precursors may be leached. Laboratory leaching of geopolymer have been conducted, but these works focus on the immobilization effects of geopolymer on artificially supplied toxic elements [9–11]. Different from being used as construction material, geopolymer-based hazardous immobilization matrixes are meant to be deposited, and the corresponding release limits are much higher. With the increasingly stringent environmental regulatory criteria for building materials, the leaching behaviour of heavy metals and trace elements from geopolymer-based construction materials should be fully evaluated before marketing. However, studies about this aspect have not been reported.

An integrated framework was applied to evaluate the leaching characteristics of geopolymeric materials. In our previous work, the leaching of major and trace elements from geopolymer mortars have been characterized in a broad pH range [14]. Geochemical modelling has been used to reveal the mineral phases that control the solubility of framework components. As part of the series study, this work is designed to reveal the environmental compatibility of geopolymer mortars by characterizing the leaching of Na, K, Al, Si, Ca, Ba, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Tl, V, Zn, chloride and sulfate from monolithic specimen. Both fly ash and metakaolin based geopolymers were used, which are the most extensively studied geopolymer binders. A commercial geopolymer was also tested. Factors controlling the leaching process were analysed. To provide a direct view on the difference of leaching characteristics between geopolymer and cement, a comparison with cement is included in this work. The leaching results are also compared with the environmental regulatory limits in Germany and the Netherlands. In addition, influences of the leaching on the mechanical and mineralogical properties of geopolymers were documented. The results from this work together with our previous and upcoming findings [14–16] contribute to promote the environmentally compatible application of geopolymer as construction material.

2. Materials and methods

2.1. Materials

Fly ash (FA) and metakaolin (MK) are used in this work as solid precursors for geopolymer synthesis. The chemical and mineralogical compositions of FA and MK are shown in the Supplementary Tables 1 and 2 as well as in the Supplementary Fig. 1. Results indicate that 73.0% and 82.4% of the FA and MK are made up by amorphous phases, respectively. The initially contained crystalline phases, such as quartz, mullite, hematite, muscovite, etc., are of small quantity.

Apart from the fly ash geopolymer (FAG) and metakaolin geopolymer (MKG), a commercial geopolymer (CG) was purchased and tested in this work. This is a ‘just add water’ geopolymer, in which the alkaline activators, fine aggregate, and chemical admixtures were premixed. The CG was sieved for analysis of physicochemical properties. The particle size distribution is shown in the Supplementary Fig. 2. Fine particles passing the 0.1 mm sieve were collected. It can be inferred from the Supplementary Tables 1 and 2 that the fine fraction of the CG is predominantly composed of Al_2O_3 and SiO_2 , with the amorphous phases accounting for 69.8%.

Solid precursors were digested in aqua regia solution to determine the content of heavy metals and trace elements. Inductively coupled plasma mass spectrometry (ICP-MS) was applied for the measurement. Results are listed in Table 1.

Sodium silicate solution, containing 23.7 wt% SiO_2 , 16.4 wt% Na_2O and 59.9 wt% H_2O , was used as alkaline activator for FAG and MKG. The activator modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio) was 1.5 M. The

Table 1

Content of heavy metals and trace elements in of FA, MK and the fine fraction of CG (particles < 0.1 mm) (given in mg/kg).

Parameter	FA	MK	Fine fraction of CG
Antimony	2.97	0.83	3.05
Arsenic	55.1	8.1	28.3
Barium	728	127	553
Lead	19.8	17.7	36.3
Boron	370	11	232
Cadmium	0.279	0.041	0.290
Chromium	35.7	72.6	45.4
Cobalt	13.3	2.9	9.8
Copper	35.4	5.6	199.1
Molybdenum	13.4	0.3	13.9
Nickel	36.0	36.5	24.6
Selenium	3.23	1.90	2.72
Strontium	838	36.6	479
Thallium	0.32	0.11	0.44
Vanadium	88.5	112.3	98.4
Zinc	46.3	29.9	46.0

selection of activator and decision of liquid/solid ratio were based on our previous work [16]. The liquid/solid ratio for FAG and MKG was 0.45 and 0.75, respectively. The corresponding water/binder ratios are 0.23 and 0.35, in which the binder refers to the solid precursors and the anhydrous activator.

Tab water was used for the preparation of CG, which accounts for 9 wt% of the solids. The water/binder ratio can be estimated to 0.33 (taking fine fraction as binder). Table 2 lists the main chemical composition of FAG, MKG and CG binders by taking the anhydrous activator into account.

2.2. Sample preparation

Mortar samples were prepared for strength measurements and the leaching experiments. The FAG and MKG binders were produced in a planet mixer. After 2 min mixing, CEN standard sand (according to EN 196-1) was added and further mixed for another 3 min. The mass ratio of sand-to-binder is 3 for both geopolymers. The CG mortar was produced at 1000 rpm for 5 min. The homogeneous fresh mortars were then casted into moulds of $40 \times 40 \times 160 \text{ mm}^3$, followed by 2 min vibration to remove entrained air bubbles.

The curing possesses significant influence on the reaction and strength development of obtained geopolymers. For example, the reaction of FAG is more temperature-dependent than MKG, and high temperature curing is normally required for FAG. The curing procedures have been extensively characterized in our previous study in a time scale of one year [16]. For the used materials, curing of FAG at 40 °C was sufficient, for other samples, higher temperatures may be needed. In detail, the FAG samples were sealed in PE bags and transferred into an oven of 40 °C, while the MKG and CG samples were cured in a curing box at 20 °C and approx. 100% relative humidity (RH). After 24 h, all samples were demoulded, wrapped by PE foil and stored at

Table 2

Main chemical composition of FAG, MKG and CG binder.

Parameter/compound	Unit	FA + activator	MK + activator	Fine fraction of CG (incl. activator)
Al_2O_3	wt%	18.36	25.06	19.05
SiO_2		53.70	60.75	56.48
CaO		4.11	0.10	3.99
MgO		1.60	0.12	1.42
Na_2O		7.19	9.59	0.31
K_2O		1.92	0.48	5.05
Al/Si	mol/mol	0.40	0.49	0.40
(Na + K)/Al		0.76	0.65	0.31

20 °C and 65% RH for another 55 days.

2.3. Horizontal dynamic surface leaching test

The horizontal dynamic surface leaching test (DSLIT) was conducted following CEN/TS 16637-2 [17]. The CEN/TS 16637-2 was developed to test monolithic samples. The material should be as close to practice as possible. AAM will be used as a binder for mortars or concretes. The use of aggregates changes the microstructure, especially in the contact zone between aggregate and paste (interfacial transition zone (ITZ)). Since leaching is often controlled by diffusion, it is important that the tested samples have a realistic microstructure, including the ITZ. Therefore mortar samples were used in these tests (instead of paste samples). Prior to the leaching test, the mortar samples were cured airtight for 56 days. Each sample was put in a vessel with screw cap. To guarantee the distance between the sample and the vessel, plastic bar spacers of 2 cm thickness were used. The water volume divided by the sample surface was 80 l/m². At fixed intervals of 0.25, 1, 2.25, 4, 9, 16, 36, and 64 days, the eluate was sampled and changed. A blank test was also conducted, in which no mortar sample was used.

After sampling, the pH value and electric conductivity of the eluates were measured. Na, K and Ca concentrations were measured using flame photometry (ELEX 6361, Eppendorf). Ion chromatography (ICS 1100, DIONEX) was applied to measure Cl⁻ and SO₄²⁻ content. The concentrations of Al, Si, As, B, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn were then measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, 5110, Agilent). Prior to the ICP-OES measurement, sampled eluates were acidified with 5 vol% supra pure nitric acid.

The normalized concentrations and the cumulative release were calculated following Eqs. (1) and (2), respectively.

$$c_{N,i} = \frac{c_i}{\bar{c}} \quad (1)$$

$c_{N,i}$ normalized concentration of interval i

$\bar{c}$ average concentration of the whole DSLIT, $\bar{c} = \frac{\sum_{i=1}^8 c_i}{8}$,

$$R_n = \sum_{i=1}^n R_i = \sum_{i=1}^n c_i \frac{V}{A} \quad (2)$$

R_n cumulative release at the end of interval n in mg/m²

i sampling period (1 to 8)

R_i release during interval i in mg/m²

c_i concentration in the eluate i in mg/l

V volume of the deionized water in l

A surface area of the sample in m²; $V/A = 80$ l/m².

In terms of quality control, two sets of double-determination were conducted for the FAG and MKG systems, i.e. four mortar samples in each system were used for leaching. For the CG system, one double-determination was applied. The obtained data from each replicate vary in a small range, thus the average results are shown here with all the raw data submitted as Electronic Supplementary file 1.

2.4. Strength measurement

After 56 d of curing, the compressive strength of FAG, MKG and CG was determined. Strength tests on samples after leaching were also conducted. The measurement was operated with a load rate of 2.4 kN/s.

2.5. XRD measurement and data analysis

After strength measurement, the surface layers exposed to leachate (ca. 0.5 mm in depth) were abraded for XRD measurement. The obtained powder was further dried in vacuum oven at 40 °C for 24 h.

Afterwards, the powders were manually ground using an agate mortar to pass through a 63 μm sieve. XRD measurements were also applied on unleached samples.

The XRD measurement was conducted using an X'Pert Pro Diffractometer (PANalytical, Netherlands). Data were collected over 2θ range of 5–60° in the theta-theta geometry. A tube condition of 40 kV and 40 mA was used to generate CuKα X-rays for the measurement. Data analysis was operated using the software HighScore Plus from PANalytical. The quantitative analysis of solid precursors was based on the Rietveld refinement. Rutile Kronos 2220 was used as internal standard, which was thoroughly mixed with precursors at a level of 20 wt% of the blend. Detailed description about the analysis procedure is also reported in [15,16].

2.6. Pore solution extraction and analysis

Pore solution was extracted from FAG and MKG pastes only. The prepared pastes were filled in 250 ml PE bottles, and rotated for 24 h to prevent sedimentation. Samples were then stored at 20 °C 65% RH for 56 days. Throughout the rotation and curing, bottles were tightly sealed to prevent carbonation. After 56 days of curing, the hardened pastes were taken out of PE bottles for pore solution extraction. The pressure used was up to 520 MPa. The collected pore solution was analysed for pH value, electric conductivity, and concentration of chemical components.

2.7. pH dependent leaching of FAG and MKG

As aforementioned, the pH dependent leaching of major and trace elements from FAG and MKG mortars have been characterized in our previous work [14]. The main findings are important for the leaching mechanism interpretation of DSLIT results. Therefore, the test method is shortly described here. FAG and MKG mortars were produced in the same mix design and curing procedure as described in Section 2.2. After 56 days curing, samples were crushed until ≥85% of the initial mass passed 2 mm sieve. Suspension was then made by mixing crushed samples with 10 times of deionized water. HNO₃ (Suprapur) or NaOH solution (analytical grade) were used to adjust the pH values of suspensions. The end-pH values ranged from 1 to 14, and the pH value of suspension without acid or base addition is referred to as “natural pH”. Electrical conductivity, pH value, concentrations of main and trace components were measured after 48 h.

3. Results and discussion

3.1. Characterization of the geopolymers before leaching

3.1.1. Compressive strength

The 56 d strength of FAG, MKG and CG is 50.1 ± 1.3 MPa, 68.0 ± 2.5 and 32.2 ± 1.9 MPa, respectively. The FAG and MKG possess better mechanical properties, which satisfy most structural application scenarios. The CG was developed for maintenance works which require lower strength, but high durability.

3.1.2. Phase composition

The XRD patterns of FAG, MKG and CG are shown in Supplementary Fig. 3. Most of the mineral phases in solid precursor remain unchanged except the anhydrite in FA and activators in CG binder (fine fraction). Reflections of these phases disappeared after reaction. Formation of Chabazite (Ca, Na₂, K₂, Mg)Al₂Si₄O₁₂·6H₂O, PDF No. 98-001-7778) was detected in CG. Chabazite is characterized by a basic framework built by the repletion of double six membered rings of Al- and Si-tetrahedra [15]. Formation of Chabazite during geopolymerization has also been detected in the investigations of [2,15]. Compared with the solid precursors, a shift of the amorphous hump to higher 2θ angles can be seen. This is assigned to the formation of new amorphous phases, a highly

Table 3
Pore solution compositions of FAG and MKG.

Parameter	Unit	FAG	MKG
pH value	–	13.7	13.4
Sodium	mmol/l	152.6	126.9
Potassium		3.8	2.5
Calcium		0.7	0.4
Chloride		4.0	3.0
Sulfate		1.9	0.9
Aluminium		7.3	10.4
Silicon		30.5	20.1
Antimony	µg/l	22.1	9.4
Arsenic		33.5	14.3
Barium		245	91
Lead		23.5	12.1
Boron		787	477
Cadmium		8.8	2.6
Chromium		366	191
Cobalt		56.1	14.3
Copper		105	77.3
Molybdenum		539	197
Nickel		51.2	29.1
Selenium		332	133
Thallium		8.3	4.9
Vanadium		1934	1215
Zinc		97.2	29.6

cross-linked alkali aluminosilicate-type gel (N(K)-A-S-(H)) [1,3]. The N(K)-A-S-(H) gel is the preliminary reaction product of the geopolymers. The reaction kinetics of FAG and MKG have been studied in [15,16]. A more significant shift can be inferred in MKG and FAG systems than for the CG, indicating a higher reaction degree of the formers. These findings are consistent with the much higher strength of MKG and FAG compared to CG.

3.1.3. Pore solution

The pore solution compositions of FAG and MKG are listed in Table 3. These concentrations not only provide a direct view of the concentrations of studied chemical components but also serve as a basis for leaching mechanism analysis. A detailed discussion is given in Section 3.2.3.

3.2. DSLT results

3.2.1. pH value and electric conductivity

The evolutions of pH value and electric conductivity are shown in Fig. 1. It can be seen that the pH values change slightly during the

DSLT. The standard deviations of the pH values (σ_{pH}) are 0.13, 0.10 and 0.14 for FAG, MKG and CG system, respectively. The FAG system exhibits higher pH values than MKG and CG counterpart. The pH values of the eluates are affected by the physicochemical properties of the solid precursors, the dosage of alkaline activator, and the reaction degree of geopolymer. Though more activator was used for MKG synthesis, the pH values are lower than in the FAG system. That can be caused by unreacted activator in the FAG system due to its lower reaction extent [16]. The CG has a lower alkali content (compare Table 2) and therefore lower pH-values.

As shown in Fig. 1(b), the electric conductivity of the eluates from FAG and CG systems are similar, especially at the beginning of the test. Both are higher than the electric conductivity in MKG system. The electric conductivity has been recommended as an indicator of total ionic strength [18,19]. It can be deduced that higher amount of ions were leached out from FAG and CG than MKG. Detailed discussions about the leaching behaviours will be given in following sections.

3.2.2. Leaching of major components

The leaching of Si and Al from the different geopolymer mortars are shown in Fig. 2. Exemplary leaching results of Al from cement systems are also shown in Fig. 2(b) for the purpose of direct comparison. Si and Al are the main framework components of N(K)-A-S-(H), the leaching behaviours of Si and Al provide valuable information concerning the stability of geopolymer binders and might be helpful in understanding the chemistry of N(K)-A-S-(H) gel. In Fig. 2(a), higher amounts of Si were leached from FAG and CG than MKG. As listed in Table 2, the highest initial content of Si was found in MKG. In addition, the higher water/binder ratio of MKG resulted in a higher porosity of the resultant geopolymer [16]. These factors seem to favour the leaching of Si from MKG. However, the high reaction degree of MKG reduces the pore solution concentration and the leaching of Si. The leaching of Al from geopolymer mortars shows an opposite tendency. The highest amount of Al was leached from MKG, while the CG released the lowest amount.

It can be calculated that the Al/Si ratios in the FAG and CG eluates are lower than the initial Al/Si ratio of the binder (Table 2). This indicates that Si is more easily leached out than Al from FAG and CG. The contrary phenomena were found in the MKG system. A study about the effect of stoichiometry on physicochemical properties of geopolymeric gels is needed to reveal the chemistry and stability of geopolymers.

Fig. 3 depicts the leaching characteristics of Na and K from FAG, MKG and CG mortars. The adoption of sodium-based activators is responsible for the higher cumulative release of Na from geopolymer than cement mortars and concretes. The highest amount of Na was released from the FAG, which is over 4 times of its MKG counterpart. The initial

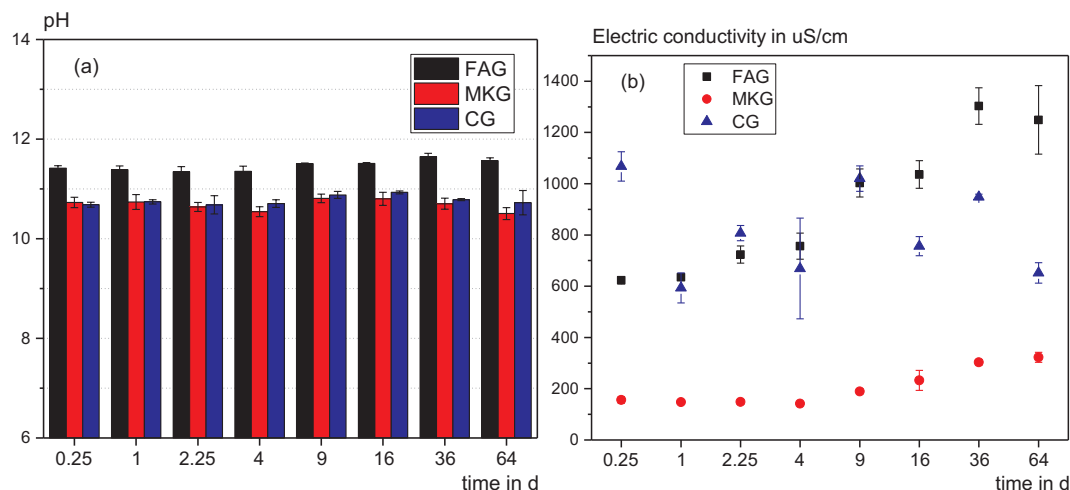


Fig. 1. PH value and electric conductivity during DSLT (whiskers: standard deviation).

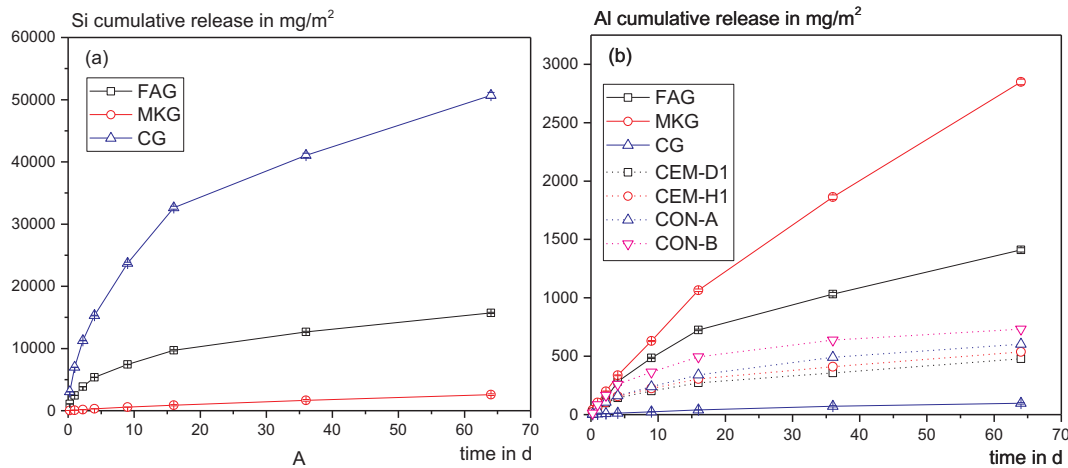


Fig. 2. Leaching of Si and Al from different geopolymer mortars in deionized water (CEM-D1 and CEM-D 2 from [18], CON-A and CON-B from [20], (no Si leaching data were reported in [18,20])).

Na content in MKG is higher (Table 4). The higher release is probably caused by the lower reaction degree of FAG, leaving more unreacted, mobile alkali in the solution. This is confirmed by the pore solution concentrations given in Table 3. The largest amount of K was released from CG followed by FAG and MKG, respectively. This behaviour corresponds to the K content in the binder.

Both Na and K possess the ability to balance the negative charge caused by the substitution of silicon by aluminium in the geopolymeric gel framework. As reported in [21,22], Na prefers to form inner surface complexes with tetrahedral charge sites in many aluminosilicate phases. The facile de-solvation property and large radius of K make it less dependent on the location of charge site. The difference in chemistry might also influence the leaching behaviours of both elements.

The leaching of Ca from geopolymer mortars are shown in Fig. 4. The highest amount of Ca was leached from CG, followed by FAG and MKG. The initial calcium content in CG is slightly lower than FAG. The role and fate of calcium during geopolymerization is still under investigation [3,28–31], further discussion is given in Section 3.2.4. In comparison, much more Ca is released from cementitious systems. This is caused by the high available content of calcium in cement. As one of the main components of cement, calcium not only takes part in the formation of reaction products in hydrated cement but also exists in pore solution of hardened cementitious materials [12,13,23]. Statistical evaluation conducted by Vollpracht et al. [23] indicates that calcium concentration in pore solution of hardened PC pastes can be up to

Table 4

Cumulative release of heavy metal and trace elements from FAG, MKG and CG into deionized water, in mg/m².

Element	FAG	MKG	CG	CEM ^a	CEM-Av ^b	German threshold ^c	Dutch threshold ^d
As	5.1	2.65	3.92	0.017–11	2	11	260
B	362	21	464	0.28–8.6	2.1	813	^f
Ba	2.83	0.6	10.91	0.59–496	45	375	1500
Cd	0.3	0.12	0.24	0.001–0.51	0.085	0.56	3.8
Co	0.82	0.43	0.47	0.036–3	1.7	8.8	^f
Cr	4.58	2.17	4.40	0.18–34	2	7.7	120
Cu	0.91	0.31	3.91	0.021–22	1.9	15.4	98
Mo	14.4	1.5	19.6	0.069–3.5	0.69	38.6	144
Ni	1.28	0.78	0.64	0.16–23	3.1	15.4	81
Pb	1.45	1.06	1.65	0.006–28	3.1	7.7	400
Sb	2.05	1.06	1.72	0.007–5.4	0.37	5.5	8.7
Se	4.18	2.51	3.13	0.1–4.3	0.4	7.69	4.8
Tl	0.65	0.45	0.54	0.004–0.66	0.19	0.88	^f
V	53	22	114	0.037–61	3.8	4.4 ^e	320
Zn	2.07	1.15	2.45	0.12–67	3.8	63.9	800

^a Leaching results of cement based materials, data from [13,20,24].

^b Average of leaching results of cement based materials, data from [20,24].

^c German threshold [25].

^d Threshold in the Netherlands [24].

^e This value is currently suspended.

^f No threshold at the time being.

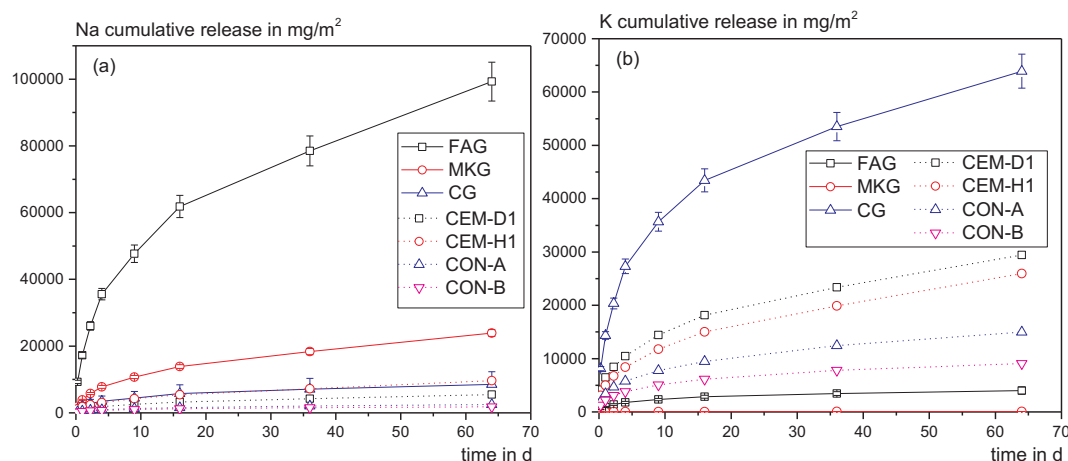


Fig. 3. Na and K release from geopolymer and cement mortars (samples with dotted lines represent cementitious binders: CEM-D1 and CEM-D 2 from [18], CON-A and CON-B from [20]).

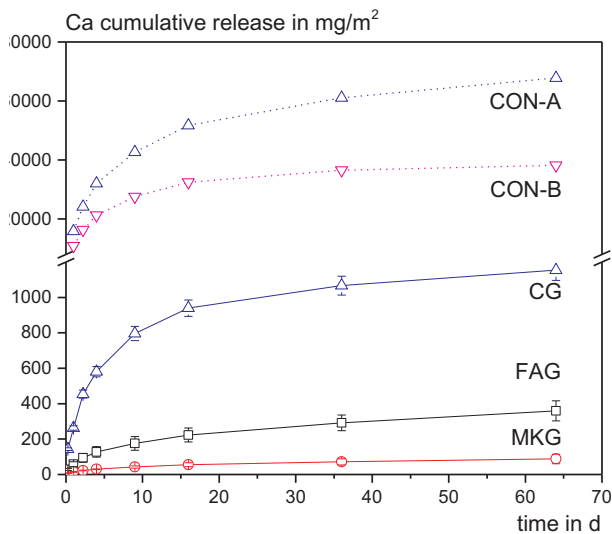


Fig. 4. Leaching of Ca from different mortars in deionized water (samples with dotted lines represent cementitious binders: CON-A and CON-B from [20]).

5 mmol/l. As shown in Table 3, lower calcium concentrations were detected in pore solutions of FAG and MKG.

Fig. 5 shows the leaching results of Cl^- and SO_4^{2-} . The leaching of both components from all geopolymer mortars behaved similarly. In general, the measured concentrations of Cl^- and SO_4^{2-} decrease during the whole DSLT, reflected as the gradually reduced increase of the cumulative release. Therefore, depletion is observed during the leaching test. Our previous work [14] has demonstrated that both components are mainly present as readily soluble species.

It should be mentioned that the binders based on Portland cement contain higher contents of SO_4^{2-} than the geopolymers produced in this work. Still, the leached SO_4^{2-} concentrations in geopolymer systems are much higher. Geochemical modelling conducted by Engelsen et al. [24] demonstrated that ettringite is the major solubility controlling phases for SO_4^{2-} at alkaline pH. This contributes to the chemical binding of SO_4^{2-} in hydrated cementitious system. Due to the low calcium content, no ettringite has been detected in geopolymers produced in this work.

3.2.3. Leaching of heavy metals and trace elements

The leaching of heavy metals and trace elements from geopolymers are important for the environmental compatibility assessment. Apart

from the above-mentioned major components Ba, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Sr, Tl, V and Zn were taken into consideration in this work. All the measured concentrations can be found in the Electronic Supplementary file 1.

In Fig. 6, the cumulative release of heavy metals and trace elements is correlated with the initial content in the binders. There seems to be a trend towards higher release with higher initial content, but not for all the studied elements. For example, the Ba content of CG is lower than of FAG, but the leaching is higher. Overall the cumulative releases of barium are low. This can be assigned to the chemical bound of Ba within geopolymer matrix due to the high alkalinity [2]. Fig. 7 exemplarily depicts the leaching behaviour of Cu, Zn, V and Mo from geopolymer mortars. The CG released the highest amount of these elements, followed by FAG and MKG, respectively. Meanwhile, the CG fine fraction contains less V than MK and less Zn than FA. In addition, the release of V and Mo are significantly higher than Cu and Zn, despite the much higher initial Cu and Zn content in all precursors. All these indicate that the leaching process is not only determined by the formulation of geopolymer binders, but also reaction degree and porosity, initial content and chemical states of elements and the pH value. Factors influencing the leaching process and potential methods to reduce the leaching of these components from geopolymers are discussed in Sections 3.2.4 and 3.2.5.

3.2.4. Leaching mechanisms

Apart from revealing the leaching behaviours of chemical components from geopolymer mortars, leaching mechanisms are also investigated. The leaching of chemicals from monolithic cementitious matrices are generally controlled by surface wash-off, diffusion, solubility or depletion [12,13]. To analyse the leaching mechanism, several methods have been put forward. In the data analysis procedure introduced in CEN/TS 16637-2 [17], the normalized concentration of each interval is calculated (see Eq. (11)). Diffusion controlled leaching is characterized by a three-step-diagram, as shown in Fig. 8(a), while a normalized concentration of approximately 1 for all leaching steps can be classified as solubility controlled. Comparison of the eluate concentration with pore solution is another way to figure out if there is a concentration gradient between the inner part of the sample and the eluate. A solubility controlled release can be assumed when the eluate concentration is in the same order of magnitude as the pore solution concentration. If there is a concentration gradient between the pore solution and the eluate, the leaching can be either diffusion controlled or solubility controlled. In the latter case, new phases must be formed on the surface of the sample, which have lower solubility than the original products [12]. In [13], success was achieved in analysing the

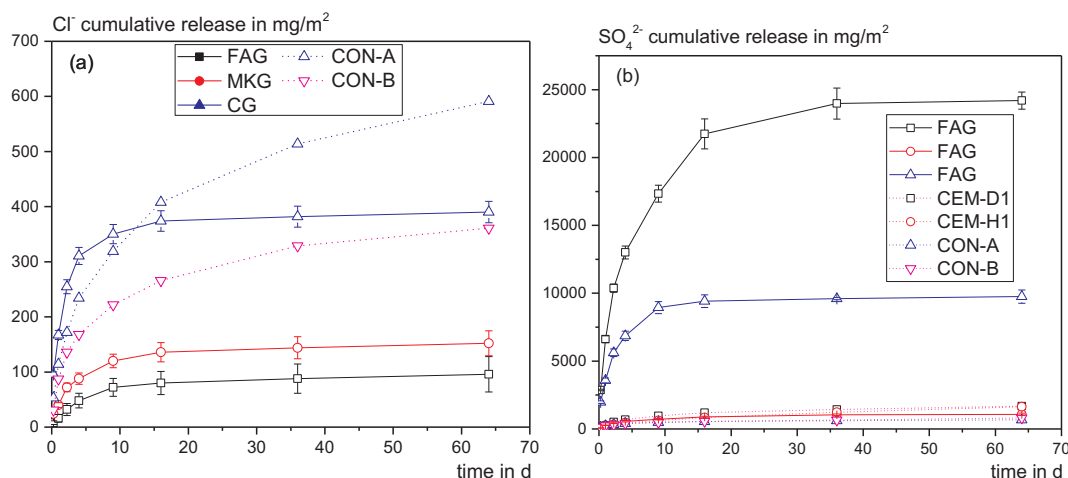


Fig. 5. Leaching of Cl^- and SO_4^{2-} from different geopolymer mortars in deionized water (samples with dotted lines represent cementitious binders: CEM-D1 and CEM-D 2 from [18], CON-A and CON-B from [20]).

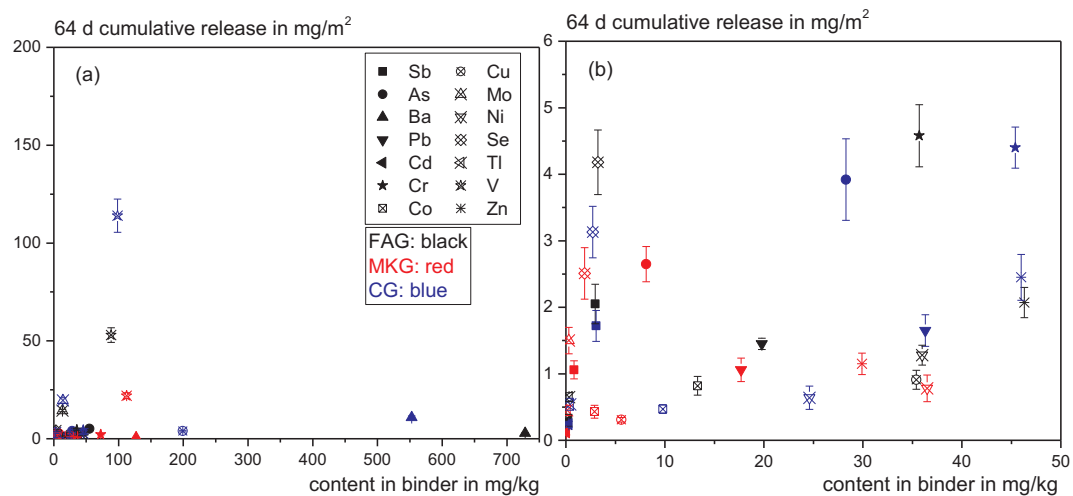


Fig. 6. Correlation of 64 d cumulative of studied components with initial content in precursor (part of figure (a) is magnified and shown as figure (b)).

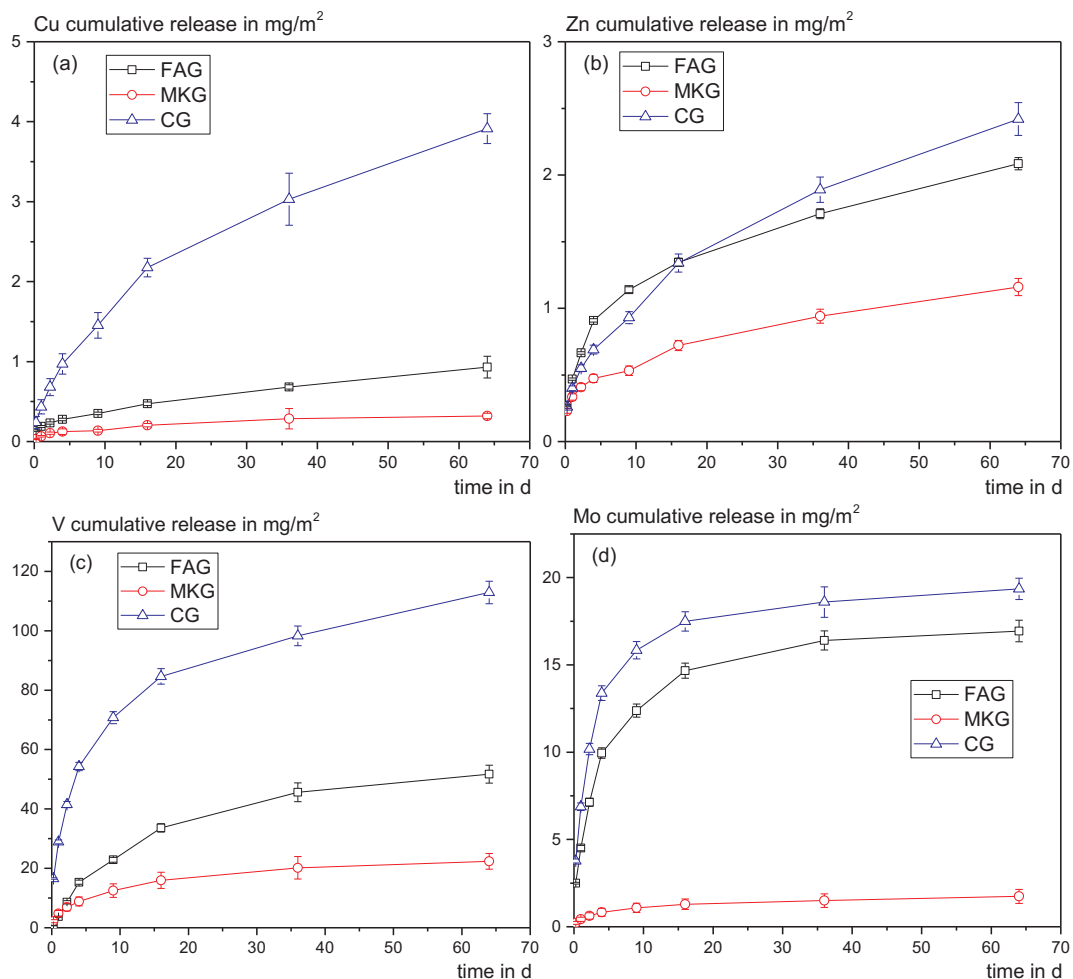


Fig. 7. Leaching of Cu, Zn, V and Mo from geopolymers in deionized water.

primary leaching mechanism via a combination of DSLT results with pH dependent leaching data. In this section, the dominant leaching mechanisms of elements leached from FAG and MKG are analysed using these methods. For the CG system, only the CEN/TS 16637-2 analysis procedure is applied due to lack of data on pore solution and pH dependent leaching. According to CEN/TS 16637-2 [17], the pH values of eluates should not change too much during the test ($\sigma_{\text{pH}} \leq 0.25$).

Otherwise, the solubility of the mineral phases changes and it is impossible to evaluate the leaching results reasonably [13]. As shown in Fig. 1(a), the standard deviations of the pH values fulfil the prerequisite.

Fig. 8 depicts the normalized concentration of Na, Ca, Si and Al from FAG, MKG and CG mortars. The normalized concentrations of Na, Al and Si from FAG, MKG and CG roughly meet the three-step-diagram

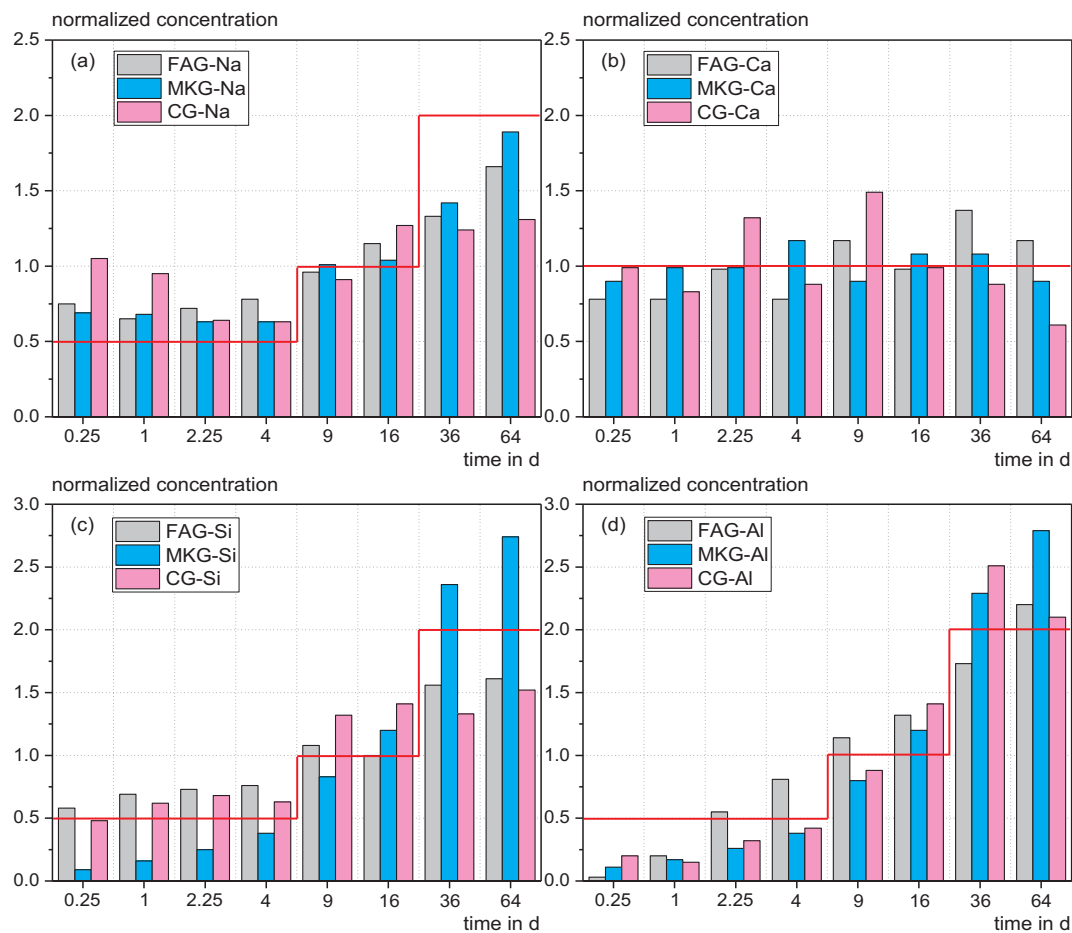


Fig. 8. Normalized concentration of Na, Ca, Si and Al from FAG and MKG mortars.

characteristic and can be regarded as diffusion controlled. In contrast, the leaching of Ca can be classified as solubility controlled. It should be mentioned that the normalized concentration of Ca from CG decreases in the last steps, indicating a depletion process. As shown in Table 2, the FAG and CG are similar in Al/Si ratio and CaO content but differ in (Na + K)/Al ratio. This may lead to a difference in the partitioning of calcium in reaction products and pore solution between FAG and CG. The role and fate of calcium during geopolymerization is not fully clear and still under investigation [3,28–31]. Calcium modified N(K)-A-S-H gel ((N,C)-A-S-(H)) was observed in Ca-poor AAM systems, and coexistence of C-A-S-H and N(K)-A-S-(H) in AAM of medium calcium content was also reported [23,28]. The formulation of the geopolymers used in this work meets the condition for the formation of (N/K, C)-A-S-(H) gel.

In Fig. 8(d), although leaching of Al can be considered as diffusion controlled following the mechanism analysis method given in CEN/TS 16637-2 (Annex B) [17], the normalized concentrations at early age are much lower than the target values while the final concentrations are higher. The leaching of Si from MKG shows the same tendency. To better analyse the leaching mechanism, the cumulative release and leaching time were plotted in log-log scale. Results are shown in Fig. 9. According to van der Sloot et al. [20], the theoretical slope of diffusion controlled leaching in the log-log plot is 0.5. This is shown as the dotted line in Fig. 9. The evaluation according to CEN/TS 16637-2 is based on the same theory, but the derived limit values for the different leaching steps do not always help to see the mechanisms clearly. The figure shows that the slopes of best fit lines of Si leaching from FAG and CG are close to 0.5, confirming a diffusion controlled leaching process. The leaching of Al from FAG at later intervals meets the diffusion controlled

characteristic but at early age the release was increasing with a steeper slope. The reason for this could be that the concentrations in the first eluates were very low. This kind of leaching is characterized as delayed release. According to [20], solubility controlling phases at the surface of the specimen that limit the release of Al in the initial stage are responsible for this phenomenon. Meanwhile, above methods cannot well explain the leaching behaviour of Si from MKG, and Al from MKG and CG. The slopes of corresponding best fit lines are larger than 0.5, indicating other factors might be involved in the leaching process. In [14], a preferential release of Si and Al from geopolymers has been observed. The difference in stoichiometry (Table 2) might affect the stability of resultant geopolymer and lead to different leaching characteristics.

The combined concentrations of DSLT, pH dependent leaching and pore solution are shown in Fig. 10. The comparison of DSLT results with pH dependent leaching helps to complement the mechanism analysis. The much lower DSLT concentrations of Na and Si from FAG and Na from MKG than pH leaching results also indicate diffusion controlled leaching characteristic. The measured concentrations of Si from MKG, Al from FAG and MKG increase with sampling time, and eluate concentrations at later periods are close to the pH dependent test results. This indicates that solubility might also be involved in the leaching of Si from MKG and Al from FAG and MKG. The different leaching behaviours of the framework components from geopolymers raise the urgency for detailed characterization of geopolymer gel chemistry.

Based on the results shown in Fig. 10(b), diffusion controlled leaching mechanism can be drawn for the leaching of Ca from FAG and MKG. This is further confirmed by the concentration gradient between pore solution and eluate. Meanwhile, this conflicts with the CEN/TS

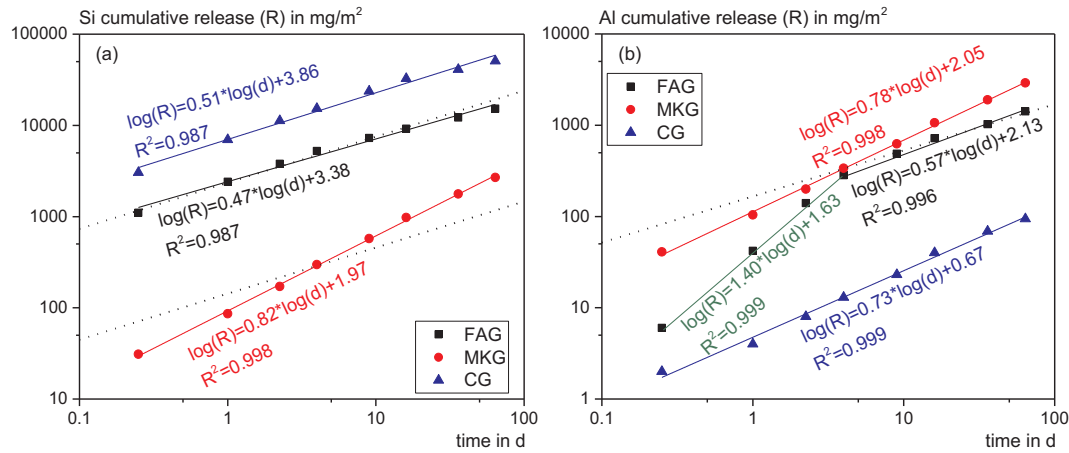


Fig. 9. Log-log plot of cumulative release of Si and Al from FAG, MKG and CG.

16637-2 method [17] (Fig. 8(b)), from which a solubility controlled leaching mechanism can be inferred. The leaching process is complex, which involves the physical and chemical properties of the solid and aqueous phases as well as the interfacial condition. Chemicals can be partitioned in reaction products, pore solution, or remain unreacted. Regardless of these, local changes of the phase composition at the surface of the specimen (for example carbonation) can also influence

the leaching.

Due to the low concentration and not fully known physicochemical properties of geopolymer, determination of leaching mechanism of heavy metal and trace elements is more problematic. Efforts are made in this work trying to discover the controlling factors. The leaching of Cu and Zn are exemplarily shown in Fig. 11(a), (b). Cu possesses a low tendency to be trapped in geopolymer matrix [2]. In [14], the lowest

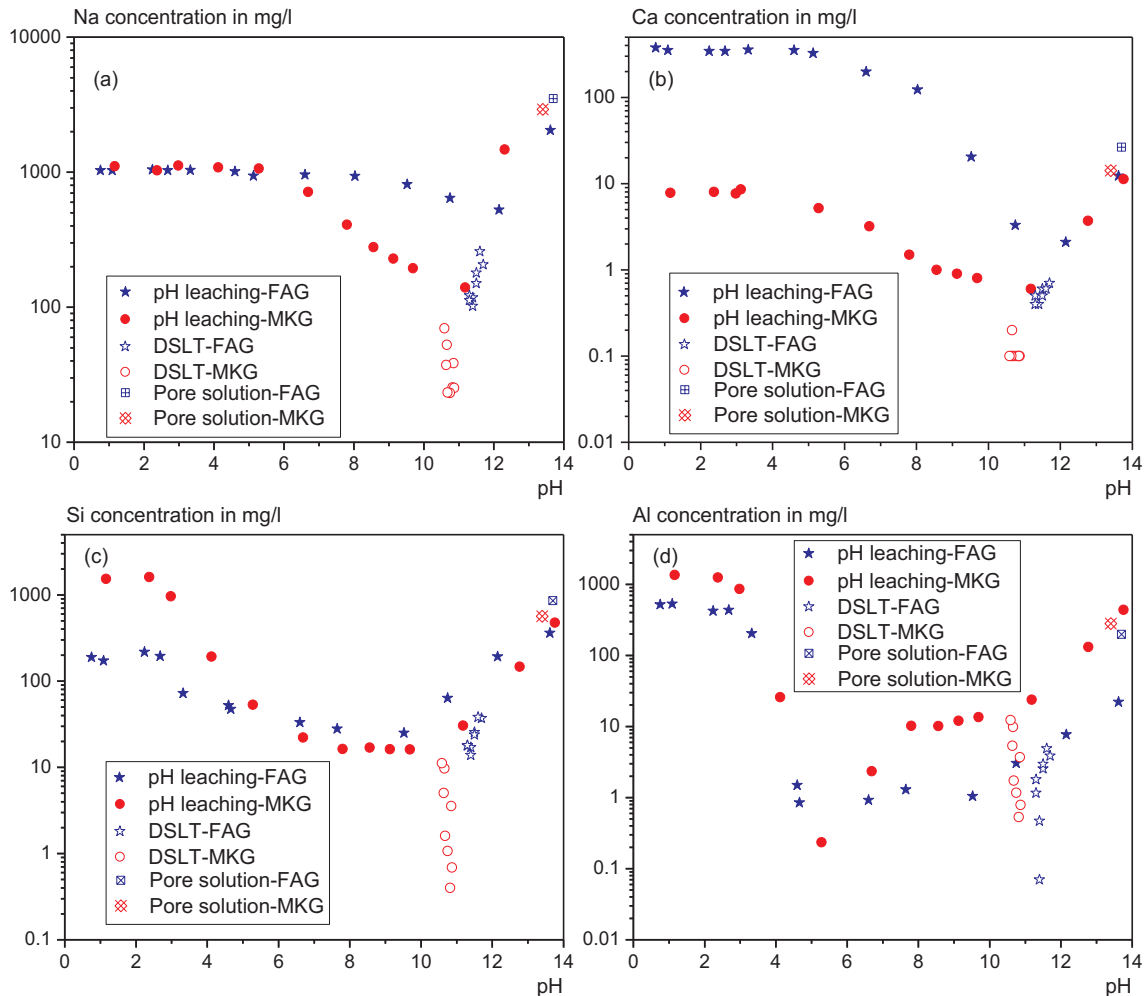


Fig. 10. Comparison of pH dependent leaching, pore solution concentrations and DSLT eluate concentrations of Na, Ca, Si and Al from FAG and MKG mortars (pH leaching data derived from [14]).

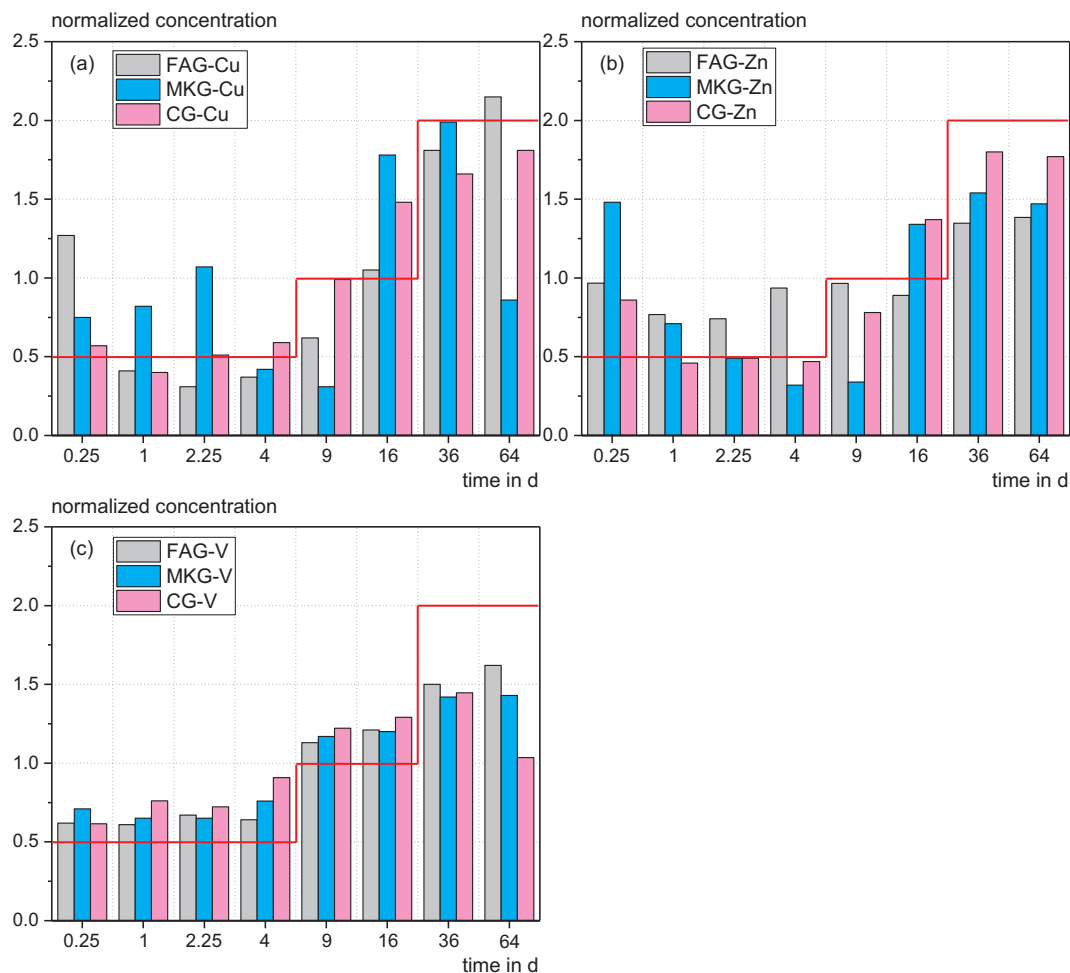


Fig. 11. Normalized concentration of Cu, Zn and V from FAG and MKG mortars.

release of Cu was found around pH 7–9, and concentration increases both in more acidic and more alkaline conditions. In contrast, Zn showed the lowest release in alkaline condition [2,14]. According to the analysis method of CEN/TS 16637-2 (Annex B) [17], the leaching of Cu from CG and Zn from FAG are diffusion controlled, while the leaching of Cu from FAG, Zn from MKG and CG are controlled by diffusion and surface wash-off. Depletion was found for Cu from MKG. The concentration gradient shown in Fig. 11(a) indicates diffusion controlled leaching characteristics.

The high release of V can be related to its high initial content in the solid precursors. In addition, V possesses a high mobility in pH 8–14, which is close to the mobility in extreme acidic region ($\text{pH} < 2$) [14]. It can be inferred from Figs. 11(c), 12(c) and Table 3 that the leaching of V from FAG, MKG and CG mortars can be classified as diffusion controlled. In Fig. 11(c), the lower final concentrations are caused by depletion.

3.2.5. Environmental compatibility evaluation

Table 4 listed the cumulative release of trace elements and heavy metals from geopolymers mortars. It can be concluded that the cumulative releases of As, B, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Tl and Zn from geopolymer are in the same range as for cement based materials. A higher release was observed for B, V and Mo from geopolymers compared to cementitious materials. This can be assigned to the oxyanionic property [14,20,24]. Compared with the thresholds, the cumulative release of most of these elements are lower than the permissible release for applications in groundwater in Germany except for vanadium (which is currently not considered). Meanwhile, the release of

vanadium from geopolymer mortars still meets the permissible release of the Netherlands.

In [24], the leaching characteristics of 167 cement-based materials were investigated. Results showed that 23% of the tested samples possess the problem of higher V release than the (currently suspended) German limit value. Though the release meets the limit values, other oxyanionic ingredients (such as B, As and Mo) also leach to a relatively high extent [24]. Artificial addition of lime in cementitious system contributes to reduce the mobility of oxyanionic ingredients [34–37]. The potential binding mechanisms include the precipitation of Ca-X-O components (X represents an oxyanionic ion), and/or coprecipitation in carbonate sites [34–37]. This offers a possible way to reduce the mobility of oxyanionic ingredients within geopolymer matrix.

3.3. Effect of leaching on material properties

3.3.1. Effect of leaching on strength

The strengths of FAG, MKG and CG mortars before and after leaching are shown in Table 5. Strength decrease can be seen in all systems after leaching. The strength loss of FAG, MKG and CG is 11.8%, 9.4% and 14.9%, respectively. Strength change of cementitious matrixes for waste solidification/immobilization after leaching has been reported in [38–40]. Deionized water not only causes the leaching of chemical components, but also influences the porosity and pore size distribution [31,32]. Choi and Yang [38] reported that the leaching increases the volume of pores, especially pores larger than 200 nm in size. All these are negative for the mechanical strength of the materials.

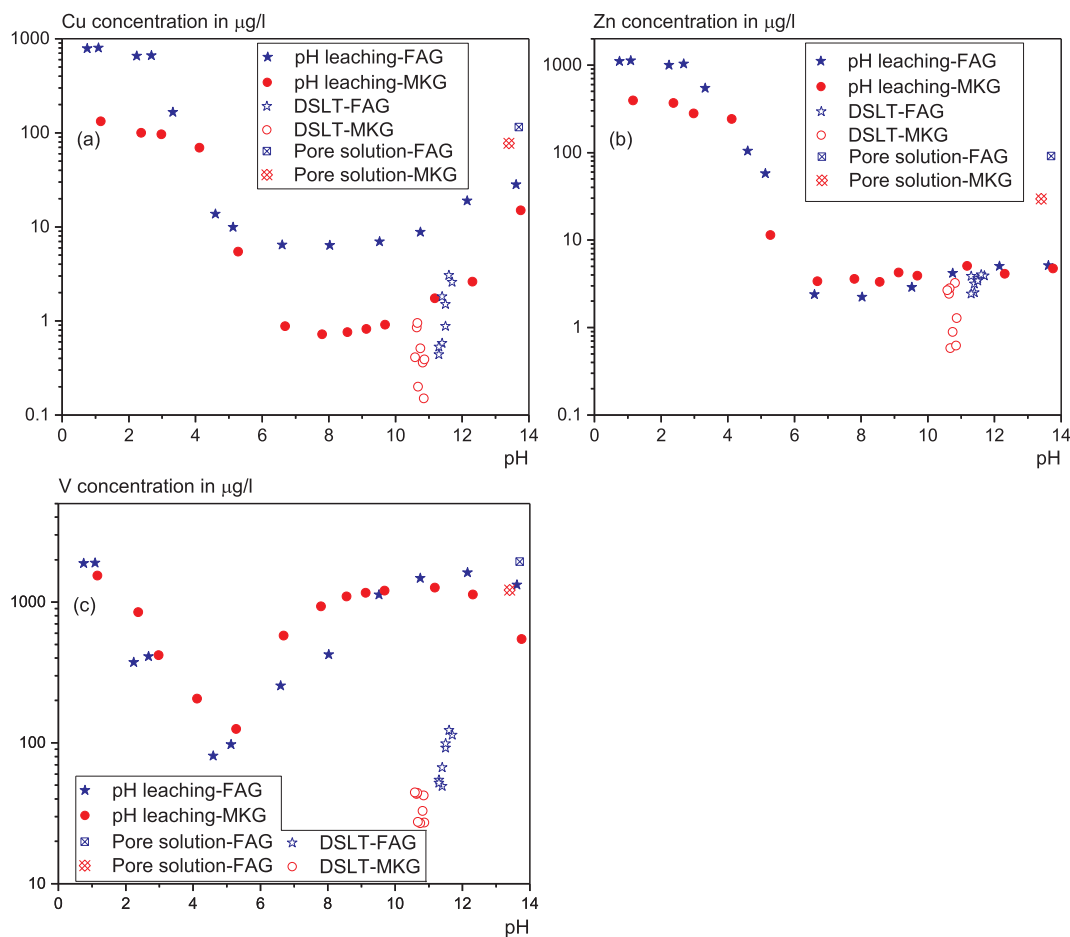


Fig. 12. Comparison of pH dependent leaching and DSLT of Cu, Zn and V from FAG and MKG mortars.

Table 5

Strength evolution of FAG, MKG and CG mortars after leaching, given in MPa.

Compressive strength	FAG	MKG	CG
56 d	50.1 ± 1.3	68.0 ± 2.5	32.2 ± 1.9
After leaching	44.2 ± 2.0	61.6 ± 3.1	27.4 ± 2.6

3.3.2. Phase composition in the surface layer

The mineralogical composition of geopolymers after leaching is shown as Supplementary Fig. 4. Compared with the un-leached surfaces, no obvious difference can be found for the surface layers of FAG, MKG and CG after leaching. Leaching of major components, heavy metals and trace elements from geopolymer mortars have been detected and discussed above. The influence on mineralogical property caused by the release of these components might be small, so that they cannot be effectively detected by XRD. More advanced technologies might help to reveal the physicochemical properties of the surface layer of geopolymers.

4. Summary and conclusion

The dynamic surface leaching of Na, K, Al, Si, Ca, Ba, As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, chloride and sulfate from FAG, MKG and CG in deionized water were studied in this work. Due to the lower reaction degree of FAG than MKG, the unreacted alkali results in higher pH values and higher release of Na in the FAG system. Si is more easily leached from CG and FAG than Al, while the highest amount of Al was leached from MKG. The cumulative releases of As, B, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Tl and Zn from geopolymer are in the same range as

cement based materials; only B, V and Mo were leached to a higher extent. The leaching mechanisms were analysed using different methods. Diffusion was found to be the predominant controlling factor. Signs of surface wash-off, solubility and depletion were also detected.

After the leaching in deionized water, strength loss of 11.8% for FAG, 9.4% for MKG and 14.9% for CG was observed. No difference was detected in terms of the phase composition in the surface layer after leaching, but further efforts are required to investigate the stability of geopolymers during leaching processes in different exposure scenarios (e.g. rain, groundwater or surface water).

CRediT authorship contribution statement

Zengqing Sun: Investigation. Anya Vollpracht: Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cemconres.2020.106161>.

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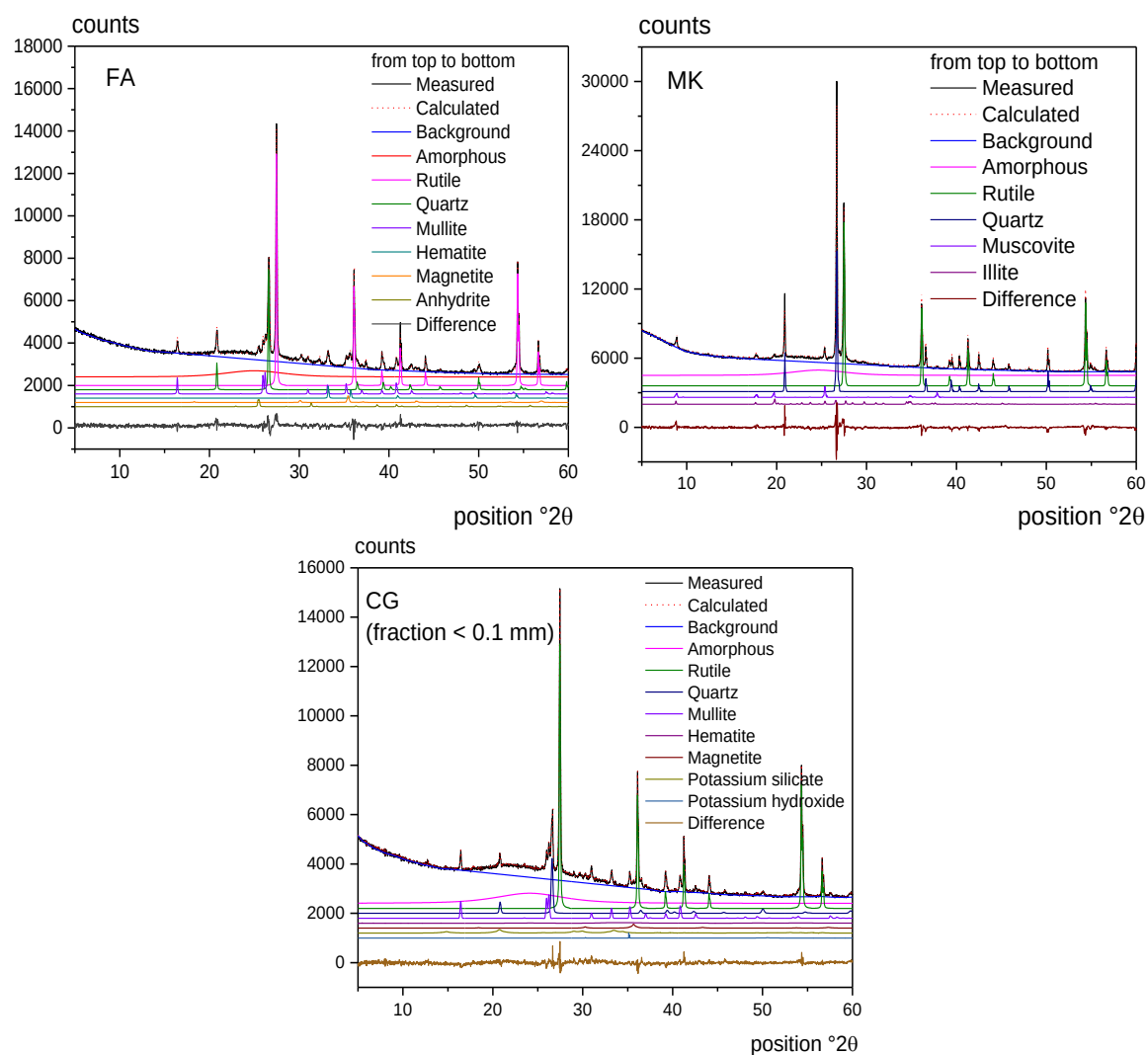
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Supplementary data 1:**Supplementary Table 1: Chemical composition of FA and MK [15], and the fine fraction of CG (particles < 0.1 mm)**

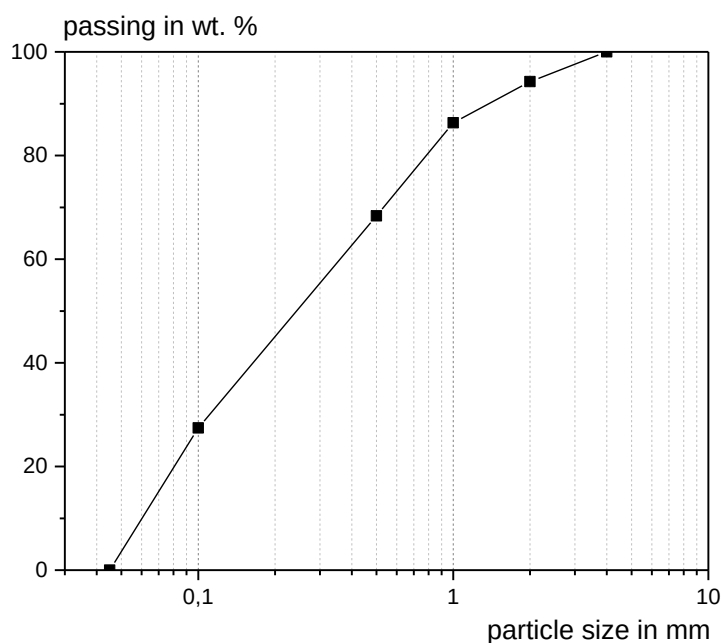
Parameter/Compound	FA	MK	fine fraction of CG
	wt. %	wt. %	wt. %
Loss on ignition	3.27	1.76	5.23
Al ₂ O ₃	21.67	32.58	19.05
SiO ₂	52.72	61.24	56.48
CaO	4.85	0.13	3.99
Fe ₂ O ₃	9.55	1.17	4.35
MgO	1.89	0.15	1.42
P ₂ O ₅	0.48	0.05	1.72
TiO ₂	0.90	1.64	0.93
Na ₂ O	1.11	0.17	0.31
K ₂ O	2.27	0.63	5.05
Na ₂ O-equivalent	2.61	0.58	3.64
Sulfur as SO ₃	1.09	0.07	1.09
Chloride	0.01	0.01	0.04
Carbon	2.30	0.03	2.02

Supplementary Table 2: Mineralogical composition of FA and MK [15], and the fine fraction of CG

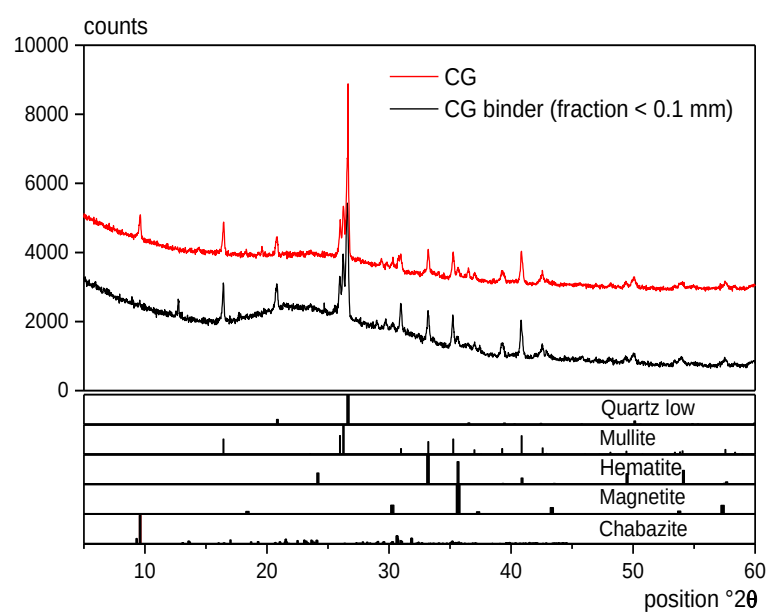
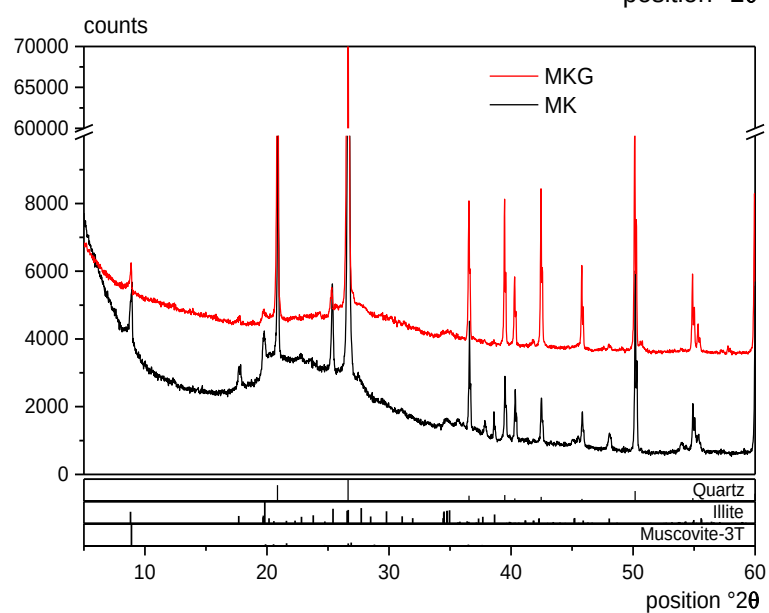
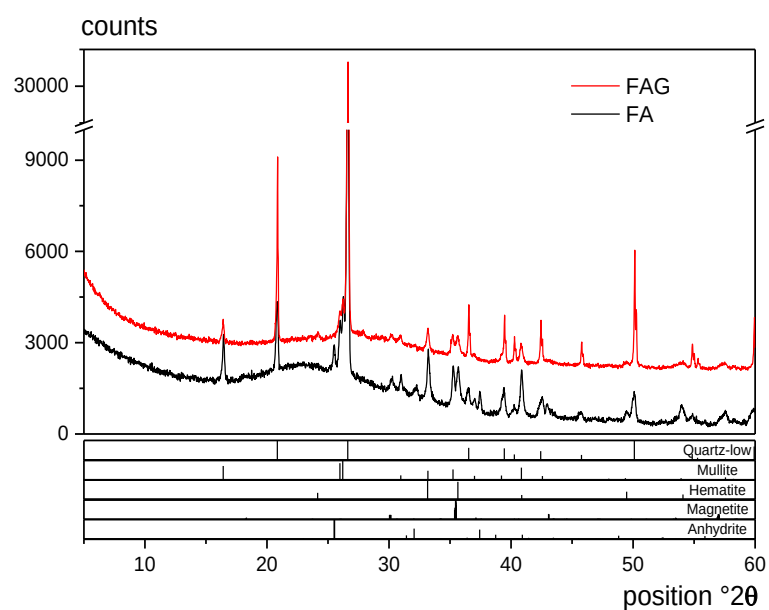
Phase	PDF-Nr.	FA	MK	fine fraction of CG
Mullite	98-008-0124	9.7	-	8.5
Quartz-low	98-005-6873	11.0	-	-
	98-002-3071	-	12.5	-
	98-010-8664	-	-	10.6
Magnetite	98-007-7842	2.2	-	-
	98-011-1284	-	-	2.3
Hematite	98-010-8081	2.5	-	-
	01-089-0599	-	-	1.0
Anhydrite	98-001-0223	1.4	-	-
Muscovite 3T	98-003-4922	-	3.3	-
Illite	98-005-6872	-	1.8	-
Potassium silicate	98-007-9416	-	-	4.7
Potassium hydroxide	00-001-1054	-	-	3.1
Amorphous	-	73.0	82.4	69.8



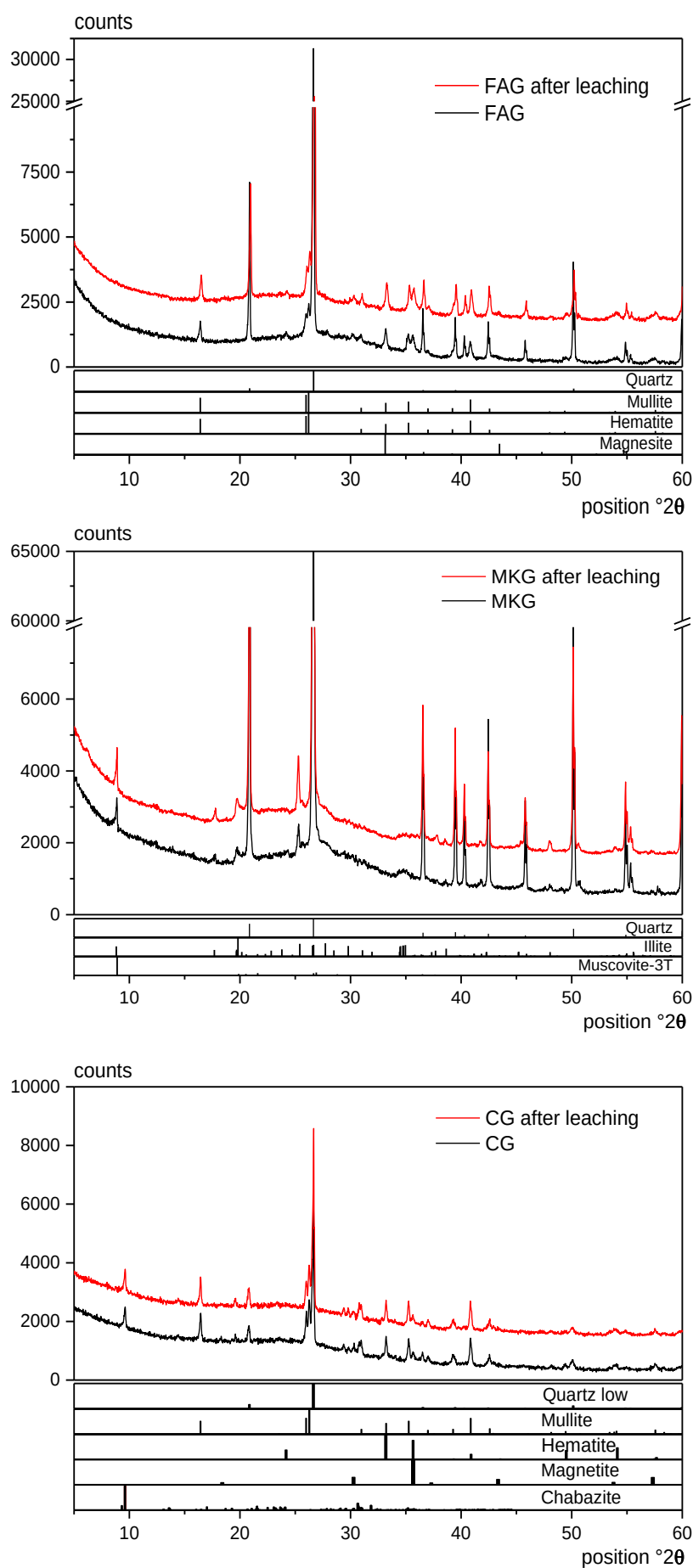
Supplementary Figure 1: XRD results of FA and MK [15], and the fine fraction of CG (rutile was added as internal standard)



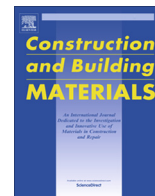
Supplementary Figure 2: Particle size distribution of the CG dry mix



Supplementary Figure 3: XRD patterns of FAG, MKG and CG



Supplementary Figure 4: XRD patterns of FAG, MKG and CG after leaching



Study of alkali activated slag as alternative pavement binder

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HIGHLIGHTS

- An alkali activated slag (AAS) was developed as alternative pavement binder.
- The AAS has similar compressive strength with cement but higher flexible strength.
- The AAS achieved comparable after-polishing skid resistance.
- The AAS mortar reduces CO₂ emission to around 40% of cement counterpart.

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ABSTRACT

The sustainable development of the building sector is an important concern of the public, industry and governments. One way to reduce the ecological footprint is to use building materials with less energy consumption and lower CO₂ emissions. In this study, a clinker-free cementitious binder was synthesized through an alkali activation of ground granulated blast furnace slag. Flexural and compressive strength of the resulting alkali activated slag (AAS) were measured and compared with ordinary Portland cement (OPC). The Aachen Polishing Machine (APM) equipped with real vehicle tires and a British pendulum tester was applied to assess the skid resistance of AAS and OPC after polishing. Reaction products were documented using the X-ray Diffraction (XRD) technique to explore the reaction mechanism. In addition, the equivalent CO₂ emission of AAS production was calculated to evaluate its environmental impact. Results show that the AAS possesses comparable after polishing skid resistance to OPC, but higher flexural strength and lower equivalent CO₂ emission. All these demonstrate that AAS can be used as an environmentally friendly alternative binder for concrete pavement construction.

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1. Introduction

Roads play a crucial role in modern civilization and will continue to be a driving force in socio-economic growth by providing increased mobility for people, goods and services [19]. Though possessing several shortcomings, such as high initial costs, higher tendency to crack and more serious noise pollution than asphalt pavement, cementitious concrete is one of the most frequently used pavement binders [44]. This is partially attributed to the high stiffness and load bearing capacity, low maintenance costs as well

as a long service life of concrete pavement [7]. However, the production of cement clinker is an energy-intensive process with high CO₂ emissions, and therefore concrete pavements are associated with a high global warming potential [17,48]. Over the years, efforts have been made to reduce the greenhouse gas emissions to promote a sustainable development of road construction. Limestone blended cement has been used in Europe for decades. Pavements using cement containing up to 10% limestone have been constructed in several states in the US [47]. According to Taylor [43], demand of ordinary Portland cement (OPC) binder can be reduced by adopting optimized aggregate gradation without sacrificing mechanical properties of the resulting concrete, but the low workability of this kind of concrete leads to a higher demand of superplasticizers. Furthermore, these concretes are less robust and the processing at varying climate conditions may be problematic [4,30]. In spite of this, work has been ongoing in

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looking for clinker-free cementitious binders, of which alkali activated slag (AAS) is a robust candidate.

AAS has received greater attention from both the academic and industrial field since the 1940s for both its comparable performance to cement binders and significant reduction of CO₂ emissions [39]. Metallurgical slags, particularly blast furnace slag, have long been used for AAS production [33]. The most frequently used alkaline activators are ROH, R₂CO₃ and R₂O·(n)SiO₂, where R is an alkali metal ion such as Na or K. The reaction processes of AAS are summarized by the destruction of the precursor, and the gelation of the dissolved ions leading to a coagulation and condensation of gels [32]. Numerous researches have discussed the superior engineering properties of AAS in detail, including rapid hardening, superior strength, resistance to chemical attack and freeze-thaw, low stringent requirements on aggregate quality, etc. [50,39,32].

Benefiting from the avoidance of high temperature sintering of carbonate precursors, which is the basic process of cement manufacturing, AAS is attributed to a small environmental footprint [15,32]. Compared with OPC, the estimated CO₂ saving property of AAS ranges from 7% to 97%, depending on the choice of mix design, curing conditions, the OPC reference and the material supply and transport [32]. Because of the aforementioned advantageous properties, AAS is among the most mature commercially applied alternative binders for high-volume infrastructure construction [11,39,32,34].

Since the 1970s, masonry blocks, workshops, retail buildings, storehouses and drainage systems have been built in the Former Soviet, China, Belgium, Finland, etc [39,33]. Particularly in Russia, several over 20 floors' residential buildings have been constructed. An inspection of these buildings conducted in 2000 revealed that the AAS based structures were in a good condition, showing no cracks or deterioration on the surface [39]. Aside from these, there are some practices of AAS in pavement construction. A 6 km trial section of high duty road was built in Russia using the blend of OPC and Na₂CO₃ activated ground granulated blast furnace slag (GGBS). After 15 years in service, the trial section exhibited very good working conditions, while those built only using OPC concrete had seriously deteriorated [39,33]. According to Mithun et al. [25,26], the AAS possess better workability, higher strength and better fatigue resistance than OPC concrete. Wu [59] and Karahan [21] investigated the polishing resistance of AAS using the ball bearing method and horizontal Böhme grinding method, respectively. Both demonstrated that the AAS retains better polishing resistance than OPC. These reported practices focused on strength development and stimulated polishing resistance of AAS binders. Studies about the skid resistance of AAS under real vehicle tires are more essential in promoting the field application of AAS in pavement construction. However, to the author's best knowledge, studies about this have not yet been reported.

Skid resistance of roads, which refers to the friction between wheels and pavement surface is essential in ensuring traffic safety because it reduces the possibility of skidding and hydroplaning of vehicles [23,18,19]. The skid resistance is intrinsically a function of material mix design and surface properties ([54,55]. Studies have shown that fine aggregate containing over 25% siliceous particles is important to withstand polishing and wearing effects over a long period of time [58]. The surface texture characteristics are known as microtexture and macrotexture [23,52]. The former refers to intrinsic fine irregularities on the surface of the aggregate particles, which contain surface asperities of less than 0.5 mm in height, while the latter involves the greater asperities that are associated with the void area among aggregates [18,53,56]). In comparison with the microtexture, macrotexture is more easily handled and can directly contribute to the dispersion of accumulated water on the road surface and the prevention of hydroplaning of vehicles [23]. Methods, such as grooving, or dragging with burlap or

brooms, which improve the surface texture of concrete pavement, are frequently used to enhance the skid resistance [3].

In this work, a clinker-free AAS was synthesized via alkali activation of GGBS. The workability was tested by measuring the setting time. Effects of activator concentration and liquid-to-solid ratio on flexural and compressive strength of the resulting AAS were studied and the reaction process was analyzed by X-ray powder diffraction (XRD). Since the AAS binder is developed as an alternative to OPC, a comparison with conventional OPC was made in the test program. The British pendulum tester and the Aachen Polishing Machine (APM) equipped with real vehicle tires were applied to assess the skid resistance of AAS. Considering the sustainable development of pavement, the equivalent CO₂ emission of AAS based paving material was calculated and compared with OPC paving. The performance with respect to mechanical properties, polishing and skid resistance, and equivalent CO₂ emission, was determined in a first test of the applicability of AAS binder from engineering and an environmental point of view. The XRD study is aimed to investigate the reaction property of AAS binder, which can offer insights into further optimizing the synthesized material. The findings of this work will contribute to the further optimization and application of AAS and other alkali activated materials in road construction.

2. Materials and methods

2.1. Materials

The GGBS and OPC used in this study are commercially available materials. The particle fineness was measured and represented by the Blaine specific surface area value, which was 4224 cm²/g for GGBS and 4290 cm²/g for OPC. The chemical compositions of solid precursors were measured using an X-ray fluorescence spectrometer (XRF) and are shown in Table 1. As expected, the GGBS has a higher content of SiO₂ and Al₂O₃ but a lower content of CaO than OPC. The mineral composition of the solid precursors was measured by powder XRD, quantitatively analyzed using Rietveld refinement and the Partial Or No Known Crystal Structure (PONKCS) method (details about the measurement and quantification are given in Section 2.2). As shown in Fig. 1 and Table 2, the OPC comprises the typical crystalline phases, alite, belite, tricalcium aluminate (C₃A) and brownmillerite. The GGBS is mainly composed of glassy structure, which is characterized by the broad hump centering at ca. 25–35 ° 2θ. Quantitative results reveal that the GGBS contains 5.1 wt% of Akermanite-Gehlenite (Al_{0.92}Ca₂Mg_{0.54}O₇Si_{1.54}) and 94.9 wt% of amorphous phase.

Analytical grade sodium hydroxides and deionized water were used to prepare the activation solution. The concentration of NaOH solution prepared was of 6 and 9 mol/L. Solutions were initially

Table 1
Chemical composition of GGBS and OPC given in % by weight.

Parameter/Compound	OPC	GGBS
Loss on ignition	1.94	0.47 [*]
Al ₂ O ₃	3.41	10.53
SiO ₂	19.91	40.28
CaO	61.29	34.54
Fe ₂ O ₃	4.80	0.39
MgO	3.72	8.63
P ₂ O ₅	0.19	0.15
TiO ₂	0.24	0.40
MnO	0.05	1.14
Na ₂ O	0.15	0.59
K ₂ O	0.43	1.62
Na ₂ O-equivalent	0.43	1.66

^{*} Tested in protective gas atmosphere.

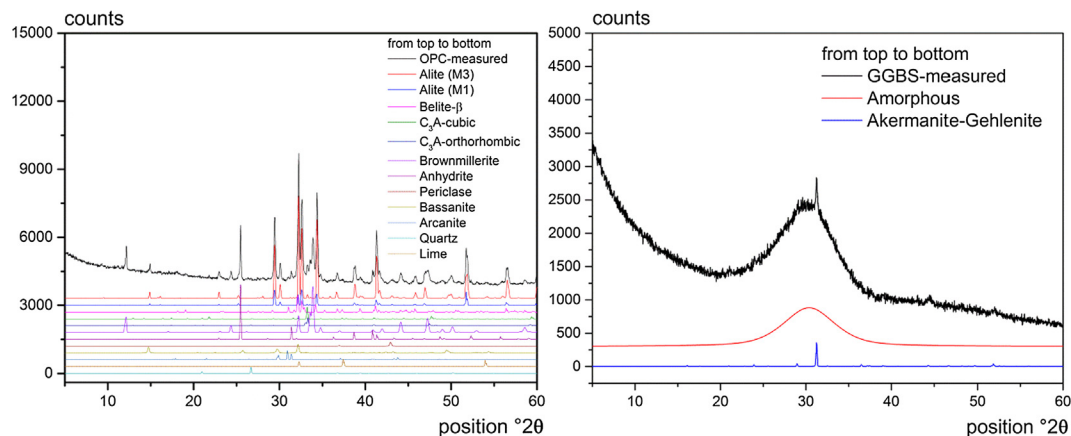


Fig. 1. XRD pattern of OPC (left) and GGBS (right).

Table 2
Mineralogical composition of OPC and GGBS.

Phase	PDF-No.	OPC wt %	GGBS wt %
Alite (M3)	01-085-1378	49.3	–
Alite (M1)	^a	9.4	–
Belite-β	98-003-4951	12.2	–
C ₃ A-cubic	^b	6.1	–
C ₃ A-orthorhombic	^c	3.2	–
Brownmillerite	98-011-4313	8.4	–
Anhydrite	98-001-0223	4.1	–
Periclase	98-011-2032	2.9	–
Arcanite	98-006-2982	1.6	–
Bassanite	98-003-3913	0.8	–
Quartz	98-005-6407	0.5	–
Free lime	98-001-1976	0.7	–
Akermanite-Gehlenite	98-011-3072	–	5.1
Amorphous	–	–	94.9

^a structure data from [29].

^b structure data from [27].

^c structure data from [28].

prepared and stored in airtight vessels at least for 24 h to cool down to room temperature prior to use.

Table 3 lists the oxide molar ratios of binders synthesized in this work. The ratios were calculated based on the chemical composition of the amorphous phase in GGBS, which was obtained by subtracting the mineral components from the bulk composition. The approach is described in further detail in [60,42]. The letters and numbers in sample ID represent solid precursor, concentration of NaOH solution and liquid-to-solid ratio, respectively. For example, GGBS-6-0.45 represents the GGBS based sample activated using a 6 mol/L NaOH solution with a liquid-to-solid ratio of 0.45. The water-to-binder ratio of OPC was 0.5.

2.2. Setting time measurement

The initial and final setting time of synthesized AAS binder (GGBS-9-0.45) and the OPC were measured using the Vicat

Table 3
Oxide molar ratios of AAS and OPC system.

Sample ID	Activator	L/S ratio	SiO ₂ /Al ₂ O ₃	SiO ₂ /Na ₂ O	SiO ₂ /(Na ₂ O + CaO)	H ₂ O/Na ₂ O	H ₂ O/(Na ₂ O + CaO)
GGBS-6-0.45	6 mol/L NaOH	0.45	6.77	4.66	0.90	14.56	2.80
GGBS-6-0.50		0.50	6.77	4.27	0.88	14.85	3.06
GGBS-6-0.55		0.55	6.77	3.95	0.87	15.09	3.31
GGBS-9-0.45	9 mol/L NaOH	0.45	6.77	3.76	0.86	10.89	2.48
GGBS-9-0.50		0.50	6.77	3.43	0.84	11.06	2.70
GGBS-9-0.55		0.55	6.77	3.16	0.82	11.20	2.91
OPC-0.5	H ₂ O	0.50	9.93	–	0.30	–	2.52

L/S: liquid to solid ratio; –: not calculated.

apparatus according to the EN 196-3. Paste was proportioned, mixed and molded into the conical ring. Instead of storing the specimen in water, the molded ring together with the base plate was placed in a curing box of 20 °C, 100% relative humidity. This can not only provide similar storing atmosphere, but also prevent the leaching of alkali medium from the paste. According to EN 196-3 periodic penetration tests were conducted by allowing a 1.13 mm Vicat needle to settle into the paste for the measurement of initial and the final setting time. For the final setting time a needle with a ring-shaped extension with a diameter of 5 mm was used in order to detect the penetration depth of 0.5 mm more accurately.

2.3. XRD measurement and data analysis

The reaction process of the selected AAS (GGBS-9-0.45) and the OPC were studied using an X'Pert Pro Diffractometer (PANalytical, Netherlands). GGBS-9-0.45 was selected because of its mechanical properties, details are given in Section 3.2. The measurements were conducted using dried powders. The reaction was stopped following the RILEM method [38]. After being cured for the specific time, pastes were crushed to the range of 125 μm to 1 mm. 3 g of the crushed powders were then mixed with 100 ml isopropanol for 15 min. The mixture was filtered and rinsed using isopropanol and diethyl ether, dried at 40 °C, and then manually ground using an agate mortar to pass through a 63 μm sieve. To quantify the phase contents, the internal standard method was used. Rutile Kronos 2220 was used as the internal standard, which was mixed with the ground powder and accounts for 20 wt% of the blend. Data were collected in the theta-theta geometry over the 2θ range of 5–60°, with the CuKα X-rays generated under 40 kV and 40 mA tube operating condition.

The quantitative data analysis was carried out using the software HighScore Plus from PANalytical. The phase content in OPC and hydrated cement samples were analyzed by the Rietveld refinement as described in [49,16]. Background was manually

set. The cell and shape parameters were initially obtained from refining the raw OPC, which were kept constant during the analysis of the hydrated specimen. The structure model of calcium silicate hydrates (C-S-H) used in this paper is the same as [16]. Cell and shape parameters, as well as the preferred orientation of portlandite ($\text{Ca}(\text{OH})_2$, PDF-No: 98-003-5154) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, PDF-No: 98-000-5652) were refined for each measurement.

For the data analysis of the AAS system, the POKCS method was applied. This method was first developed by Scarlett and Madson [37] with the purpose of quantifying the content of amorphous phases. POKCS combines the profile summation method with the Rietveld method, which has widely been used in quantifying the reaction degree of supplementary cementitious materials (SCM) in blended cement and the alkali activation process (e.g. [57,41,42]). In this research work, the amorphous profile of GGBS was derived by inserting and fitting a (*hkl*) phase to the hump in the XRD pattern. The scale factor and profile parameters were then refined. The free lattice parameter was given while refining the phase position of the inserted (*hkl*) phase. The amorphous pattern of calcium aluminosilicate hydrates (C-A-S-H) was derived in a similar procedure, more details can be found in [42].

2.4. Sample preparation for mechanical testing

Fresh AAS and OPC mortars were made by mixing weighted source materials in a planet mixer, with a constant sand-to-binder ratio of 3. The binder composition is given in Table 3. CEN standard sand according to European standard EN 196-1 [8] was used. The 5 min mixing process was followed by casting the mortar into molds ($40 \times 40 \times 160 \text{ mm}^3$ for strength measurement) and a 2 min vibration to remove entrained air bubbles. The molds were covered with a glass plate and subjected into a curing box with a temperature of 20°C and a relative humidity of 100%. After 24 h, all samples were demolded, wrapped in PE-foil and cured at 20°C and 65% relative humidity until the strength measurement.

For the skid resistance tests, plates of $40 \times 90 \times 160 \text{ mm}^3$ were made following the same procedure as described above. The surface texture was provided after vibration using a self-made steel rake. The width and depth of the groove was 0.6 mm and 5 mm, with a spacing of 20 mm.

2.5. Strength measurement

At an age of 3, 7, 14 and 28 days, flexural and compressive strength were measured following DIN EN 196-1. The flexural strength was documented using the three point loading method,

the distance between the supports was 100 mm and the load was applied at mid span. Three mortars were tested for the flexural strength, and the compressive strength was measured using the resulting six halves. The force was applied at rates of 0.05 kN/s and 2.4 kN/s for the flexural and compressive strength measurement, respectively.

2.6. Polishing test using APM and skid resistance measurement

The APM equipped with real vehicle tires, as shown in Fig. 2, was applied to polish the AAS and OPC plates. This kind of polishing can better represent the undergoing of pavement surface than other reported simulated polishing protocols, since the APM can exert three-dimensional shear stresses from translational and rotational motion. In addition, the intensive polishing conducted by APM, though in short time, can well represent the status of pavement after a long term in service [51–53,55].

The tires used were Vanco-8, 165/75 R 14C 8PR 97/95 R TL from Continental with an inner pressure of 0.2 MPa and an imposed load of 200 kg. AAS or OPC plates were fixed onto the sled and subjected to the superimposed three-dimensional shear stresses from translational and rotational motion as in reality. The translational motion was realized via the horizontally movable sled, while the rotational motion was accomplished by rotating the vertical axle connecting the tires. The horizontal back and forth movement of the sled and the spinning rate of the tires were 9 times and 41 rotations per minutes. Quartz powder with an average size of 0.04 mm was used as polishing agent, which was evenly spread over the plates with water. The polishing time for the plates varied for the different testing times. The polishing time of the plates stored for 3, 7 and 14 d was 30 min. The samples with an age of 28 d were polished for 300 min in 4 stages.

The skid resistance was measured at the end of each polishing stage using the British pendulum tester. This testing procedure has been standardized in ASTM E303 [2]. A rubber slider of given mass is attached to the end of the tubular, which can rotate around a spindle connected with a vertical pillar. Each time the rubber slider strikes the sample at a constant velocity, since it is released at the same horizontal position. The energy loss when the rubber slider is propelling over the specimen surface can be measured by documenting the travelled distance of the slider. The measured values are reported as British Pendulum numbers (BPN). A high BPN reflects that the specimen surface has high skid resistance, and vice versa. This method has been widely used for both laboratory and field tests on flat surfaces, as well as for polished stone value (PSV) measurements.



Fig. 2. The Aachen Polishing Machine.

2.7. Equivalent CO₂ emission calculation

AAS is known for its environmentally friendly properties in reducing CO₂ emission and lowering energy consumption. The equivalent CO₂ (CO₂-e) emission for the production of 1 m³ NaOH activated GGBS paving was calculated and compared with cement paving of comparable strength. Calculation was conducted following the methodology described by Turner and Collins [46], in which the CO₂-e was the cumulative contribution of different global warming gases (CO₂, CH₄, etc.) and gases generated by energy expending activities throughout the mining, processing and transport of raw materials, manufacturing and production of paving.

The cement used for comparison is of Type I (OPC) without admixture of SCM. Life cycle inventories of cement, sand and NaOH have been reported by various authors and are available in many databases [14,15,24]. The allocation of CO₂-e for GGBS is conducted based on market price by regarding the slag as the by-product of iron extraction in blast furnace [6].

3. Results and discussion

3.1. Setting time

Table 4 shows the initial and final setting time of the selected AAS binder and the OPC used in this work. The initial and final setting time of the AAS binder is 80 min and 110 min, which meet the requirement of DIN EN 197-1 for application as cementitious material. According to Bernal et al. [5], the setting time of NaOH activated binder is mainly influenced by activator concentration, and increasing NaOH concentration results in the decrease of setting time. Though not exactly measured, the other groups of AAS binder showed similar or even better workability.

Compared with the OPC counterpart, the initial setting time of AAS is much shorter, which might hinder the cast-in-situ application. Short transportation distances will be needed. Meanwhile, a small time interval between the initial and final setting time of AAS is inferred from Table 4, indicating that the AAS hardens and gives rise to strength rapidly after the start of setting. This demonstrates that the AAS binder possesses notable advantage for the production of precast concrete paving units.

Table 4
Initial and final setting time of selected AAS and OPC, given in min.

Binder type	Initial setting time	Final setting time
AAS (GGBS-9-0.45)	80	110
OPC	150	275

3.2. Reaction property

Fig. 3 compares the reaction of OPC and AAS. Most of the inherent minerals of OPC participated in the hydration, which is reflected as the decrease of intensity. New peaks representing the formation of hydration products can be seen. The reaction products include C-S-H, portlandite and ettringite. Both portlandite and ettringite are better crystallized than C-S-H. The C-S-H phase mainly centers around 26–37° 2θ (shadowed part in Fig. 3(a)). Different from the crystals in cement, the akermanite-gehlenite in GGBS is unlikely to undergo alkali activation, since it remains unchanged after 28 day curing. During the alkali activation, the amorphous was significantly dissolved. New reflections at around 7°, 29°, 32–33°, 38–39°, 50° and 55° 2θ represent the formation of C-A-S-H. Apart from this, formation of hydrotalcite can be seen in the XRD patterns of AAS.

Fig. 4 depicts the quantified results of both reaction systems. To make Fig. 4(a) look clear and concise, only the typical main phases are shown. It can be inferred that the minerals in OPC possess different reactivity. Alite and C₃A dissolve more rapidly than belite and brownmillerite in the early age of cement hydration. New hydration products are formed when the concentration of dissolved ionic species reach a supersaturation. The largest amount of reaction product is C-S-H, followed by portlandite and ettringite.

Similar to the rapid dissolution of alite in OPC hydration, the amount of amorphous phase in GGBS decreased significantly. The predominant reaction product of AAS is C-A-S-H, with the hydrotalcite as a secondary product. For both reaction systems, the formation of reaction products continues with time but slows down after 3 days.

The C-S-H and C-A-S-H are the main reaction products and are reported to be responsible for most of the engineering properties for the corresponding system. Nevertheless, the C-A-S-H is different from C-S-H in both composition and microstructure [32]. The microstructure of C-S-H gel is reported to be similar to tobermorite, which includes layers of tetrahedrally coordinated silicate chains with a dreierketten structure [36]. Though regarded as an aluminum substituted C-S-H phase, the extent of aluminum replacement in C-A-S-H gel is confined by chemical limitations imposed by the constraints of the defect tobermorite structure, and substitution predominantly takes place in the bridging tetrahedral sites [35,32]. According to the experimental and computational study by Puertas et al. [35], the C-A-S-H gel is much denser packed than C-S-H, which gives rise to the excellent mechanical properties of AAS.

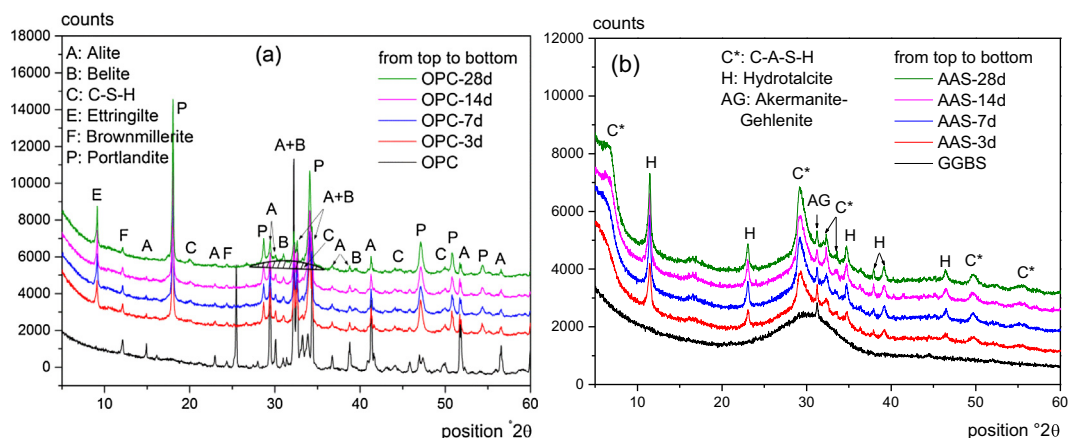


Fig. 3. Reaction products of (a) OPC hydration and (b) AAS.

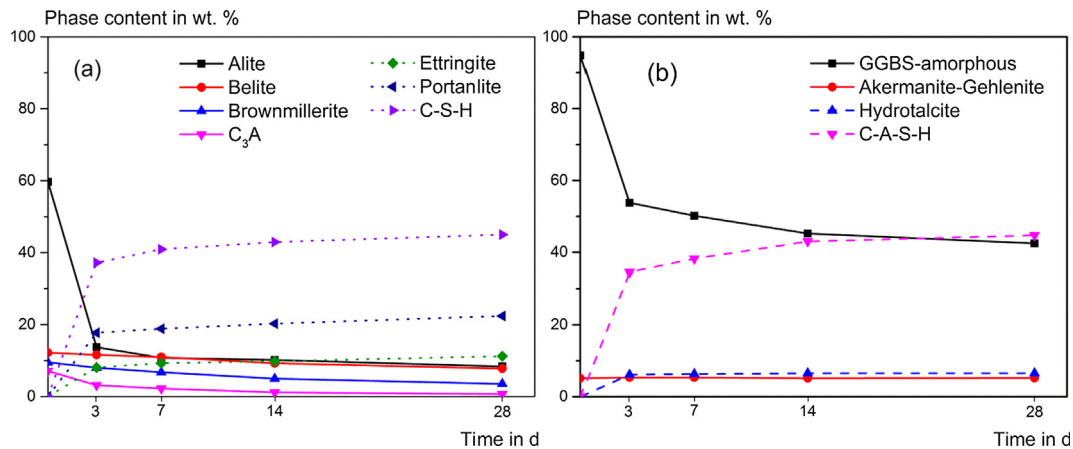


Fig. 4. XRD quantification results of (a) OPC hydration and (b) AAS.

3.3. Flexural and compressive strength

The design of cementitious concrete pavement relies upon the mechanical properties as the primary factor. The flexural and compressive strength of AAS and OPC mortars are shown in Fig. 5. The 28 d flexural strength of OPC mortar was 7.9 MPa, which meets the requirements of the Chinese standard [20] for the construction of heavy duty concrete pavement. This demonstrates the selection of this OPC is proper and meaningful. It can be inferred from Fig. 5 that both increasing the solution concentration and decreasing the liquid-to-solid ratio contributes to the flexural and compressive strength gain of AAS pavings. The sample synthesized using 9 mol/L NaOH with a liquid-to-solid ratio of 0.45 (GGBS-9-0.45) achieved the highest flexural and compressive strength. In Fig. 5, similar compressive strength gains between GGBS-9-0.45 and OPC can be seen. The strength increases in a similar way as the formation of C-S-H and C-A-S-H shown in Fig. 4. The reaction process of AAS is multistep but can be simplified as the dissolution of Ca, Si and Al from GGBS, reorientation and interaction of dissolved species, and condensation [11,22]. An activator of high concentration can accelerate the breakdown of the prime material into low stable structure units for the following reactions, which is essential for the formation of strength. Nevertheless, it has been reported that activators of excessively high concentration have negative effects on the strength gain of AAS. The solubility of calcium is reduced at a higher pH, which consequently influences the overall extent of reaction [12,32]. In addition, a solution of

higher concentration is not recommended since the production of alkali hydroxides is energy-intensive and generates large amounts of CO_2 [32], which will consequently curtail the environmentally friendly property of AAS. Though increasing the liquid-to-solid ratio also supplies more OH^- for the reaction system, the corresponding water content is also increased, as shown in Table 3. This consequently affects the gelation and condensation process of the dissolved species [39]. The increased porosity caused by a higher liquid-to-solid ratio also results in the decline of strength [31]. As a result, the GGBS-9-0.45 was chosen for the comparative study with an OPC sample in this study.

The flexural strength of GGBS-9-0.45 was 7.1 MPa at an age of 3d and increased further to 10.6 MPa after 28 days of ambient curing. As reported, the cracking and deflection behaviors of concrete pavement depend on flexural strength [7,40]. A superior flexural strength of AAS reveals a higher capacity to withstand bending damage and might contribute to decrease the fatigue rate of pavement. In addition, both the 3d flexural and compressive strength of GGBS-9-0.45 are much higher than its OPC counterpart. The high early strength property of AAS meets the needs to minimize traffic control and provides an effective solution for early opening of traffic.

3.4. Skid resistance after polishing

Skid resistance is important to ensure traffic safety, since inadequate skid resistance will lead to increased incidences of skidding

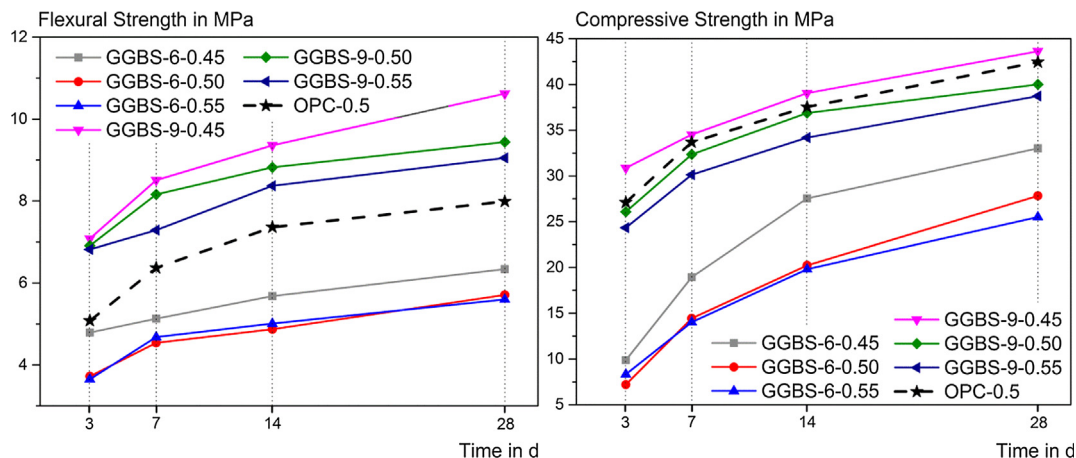


Fig. 5. Flexural and compressive strength of NaOH activated GGBS.

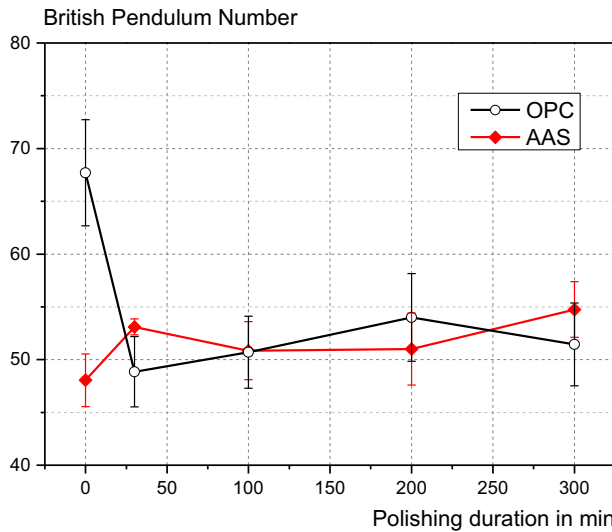


Fig. 6. The BPN values of the specimens cured for 28 days after different polishing duration.

and hydroplaning of vehicles. Fig. 6 depicts the effect of polishing time on the skid resistance of 28 days cured AAS and OPC paving plates.

It can be seen that the OPC sample possesses higher initial BPN than AAS, but after 30 min of polishing using APM, the BPN of both materials are similar. This demonstrates that AAS and OPC samples have similar skid resistance after opening to traffic. The slight increase of BPN of AAS can be attributed to the differential polishing mechanism of pavement [10]. As Tourenq and Fourmaintraux [45] stated, the soft materials in pavement are being attacked more than the hard particles during polishing. The differential relief of soft and hard materials results in a rough surface and contributes to the skid resistance. Though similar differential polishing takes effect on an OPC sample, the insufficient bonding between the OPC binder and sand might account for the BPN decrease of OPC specimens after 30 min of polishing. Considering that the after polishing skid resistance is more significant than the initial value for pavement [9,51], attention is focused on the evolution of after polishing BPN of AAS and OPC specimens.

When further extending the polishing duration, the BPNs of both AAS and OPC samples fluctuate but tend towards stability around the same level. The results prove that after opening the road to traffic and a long term in service, pavement constructed using the AAS pavement produced in this work possessed comparable skid resistance with OPC. Thus, the AAS has the potential of replacing OPC in the equivalent service conditions. In addition, the polishing span of 30 min was then adopted in the following study.

The after polishing skid resistance of AAS and OPC specimens cured for a different amount of days was studied and is shown in Fig. 7. According to the FGSV (FGSV [13], a after polishing BPN higher than 50 (dashed line in Fig. 7 is a mandatory compliance of building materials used for construction of pavement surface layers. It can be seen from Fig. 7 that the 3, 7 and 14 days cured AAS samples achieved similar after polishing BPN as the 28 days cured samples. All the measured after polishing BPN values meet the compliance, demonstrating that the AAS paving manufactured in this work has acceptable skid resistance for road surface construction, and can contribute to the early opening of traffic. Though the early age cured OPC samples acquired slightly higher BPN under the same polishing procedure, the after polishing BPN of 28 days cured OPC decreased significantly. Reasons for this phenomenon deserve further investigation.

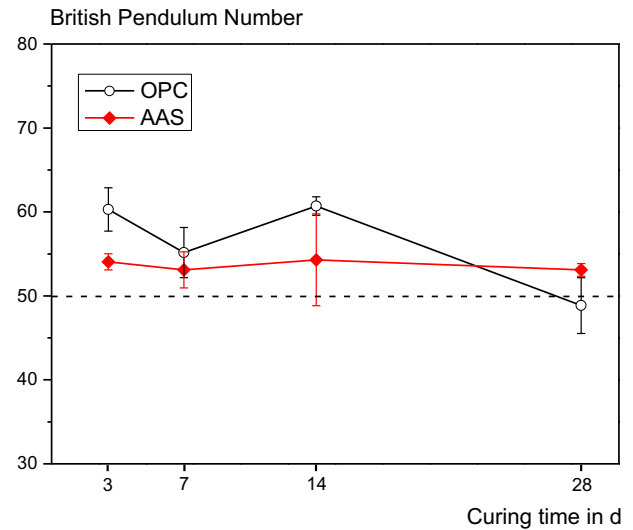


Fig. 7. The after polishing BPN values of 3, 7, 14 and 28 days cured AAS and OPC specimens.

Moreover, the BPN threshold level given by FGSV is based on building materials containing coarse aggregates. Our previous studies [51,53,54] have shown that the coarse aggregates contribute the most to the skid resistance of pavement. Adding coarse aggregate into asphalt or cement concrete can significantly improve the skid resistance of resulting construction materials. This indicates that the AAS based concrete might be promising and comparative in pavement construction. Numerous studies have reported about the polishing and skid resistance of asphalt pavement [1,51,55]. But all these focus on the properties of asphalt concrete containing coarse aggregate. A comparison with asphalt pavement will be conducted based on AAS concrete in our further work.

3.5. Equivalent CO₂ emission

To assess the environmental impact of the AAS synthesized in this work, the equivalent CO₂ emission was calculated and compared with OPC, since both are of the same compressive strength grade. Fig. 8 shows the boundary of this calculation. The functional unit of this cradle to gate study is 1 m³ AAS or OPC paving. Activities associated with the manufacture of raw materials and the production of cementitious pavements are taken into consideration. This kind of analysis is useful for construction materials of multiple applications in civil engineering and also applicable to be extended for complete life cycle assessment (LCA) of specific end-products, such as beams, pillars, pavements, houses, bridges, etc.

The mixture proportions for the production of 1 m³ AAS and OPC paving are listed in Table 5, as well as the CO₂-e data for 1 kg of related components.

Motivated by other studies [15,24,46], the effect of water was excluded from this calculation because of its extremely low environmental footprint, which makes an ignorable contribution. It should be noted that methods have been developed to allocate the environmental impact of GGBS, though no specific method seems to be fully adequate [6]. The allocation based on the economic value reflects the reality of industrial process and is used in this work. The CO₂-e emission of batching, transport and placement during paving production were taken from literature [14], which is 3.3, 9.4 and 9.0 kg CO₂-e/m³ paving, respectively. The values were first reported by Flower and Sanjayan [14] based on a six month field survey, and are nowadays widely accepted.

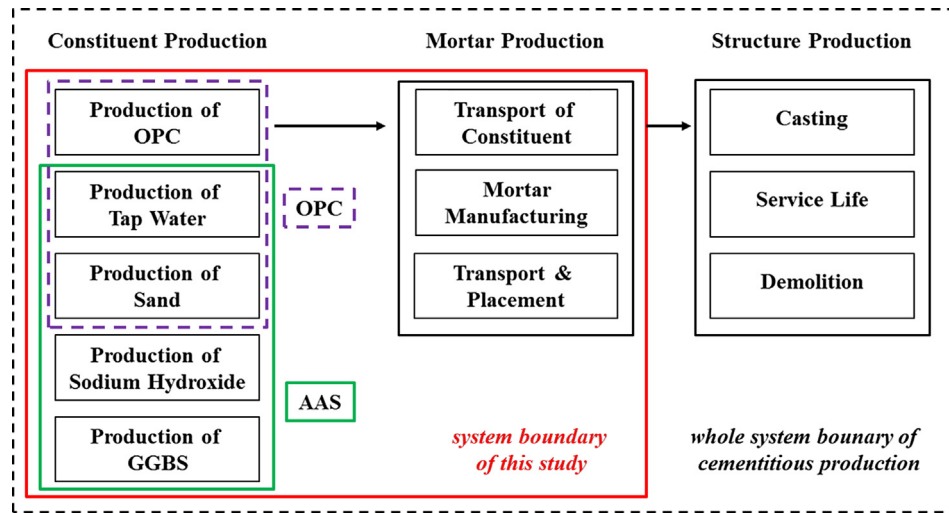


Fig. 8. Schematic boundary for life cycle assessment of AAS and OPC paving.

Table 5

Mixture proportions for AAS and OPC paving.

Material	CO ₂ -e (kg/kg)	Mixture proportions (kg/m ³)	
		AAS	OPC
GGBS	0.158	585.9	–
OPC	0.82	–	549.3
NaOH(s)	2.24	73.3	–
Water	1.55·10 ^{−4}	190.4	274.7
Sand	1.39·10 ^{−2}	1757.8	1647.9

Fig. 9 shows the CO₂-e contribution from each of the related activities and materials to the manufacture of 1 m³ paving. The total CO₂-e of AAS paving is 302.8 kg/m³, 54.2% of which was contributed to an alkaline activator. In contrast, the OPC counterpart emits 494.9 kg CO₂-e/m³ paving. In the OPC system, cement accounts for an overwhelming part of total CO₂-e. Compared with OPC paving of similar mechanical properties, the AAS system can reduce CO₂ emission by around 40%, which further demonstrates its environmentally friendly properties. According to Turner and

Collins [46], coarse aggregate contributes ca. 15% of the total equivalent CO₂ emission of both geopolymer concrete and OPC concrete. With a similar binder / aggregate proportion, the AAS concrete based on the binder developed in this work is believed to own advantages over its OPC counterpart.

4. Conclusion and outlook

In this study, the suitability of NaOH activated GGBS as an alternative pavement binder compared to OPC in terms of flexural and compressive strength, skid resistance, as well as equivalent CO₂ emission was studied. Results showed that the synthesized AAS possesses higher flexural strength than OPC of the same compressive strength grade, indicating a higher capacity to withstand bending damage. Moreover, the strength gain of AAS is faster, which might contribute to minimizing traffic control caused by construction. The AAS paving achieved comparable after polishing BPN to OPC, both meet the mandatory compliance given by FGSV for the construction of pavement surface layers. The after-polishing BPN values of AAS paving are more stable in terms of curing time and polishing duration, which can contribute to the early opening of traffic.

The main reaction product of AAS is C-A-S-H gel, which gives rise to the excellent mechanical properties of AAS. Considering the increasing environmental burden of the OPC industry, the environmental benefits of using AAS as pavement binder have also been studied by calculating the equivalent CO₂ emission of AAS paving, which reduces CO₂ emission to around 40% of its OPC counterpart. All these results demonstrate that AAS can be used as an environmentally friendly pavement binder.

The authors are highly aware that though the AAS binder possesses engineering and environmental advantage over OPC, much work is still required to reveal the other properties of the AAS binder, such as the restrained shrinkage, volume stability, moisture susceptibility, etc. Also the economic situation has to be evaluated. During service life of AAS, carbonation and weathering will take place. Future work will also extend the study to incorporate the durability of AAS concrete. Results obtained from this series of studies will contribute to evaluating and optimizing the applicability of AAS in road construction.

Conflicts of interest

None.

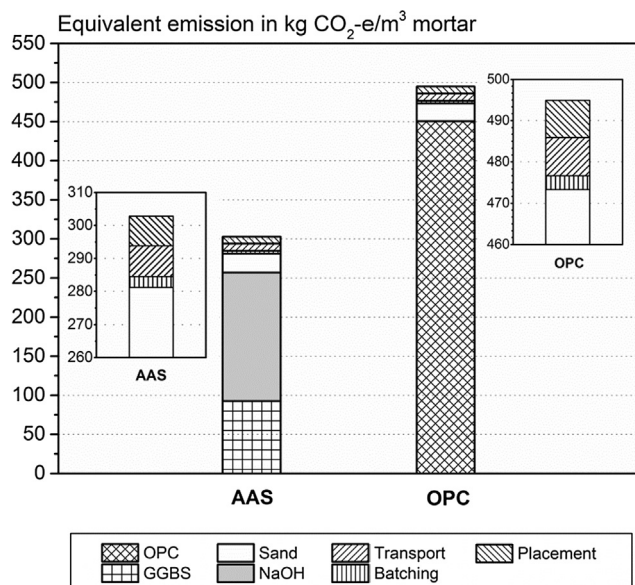


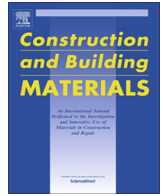
Fig. 9. CO₂-e emission of AAS and OPC paving.

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Pervious concrete made of alkali activated slag and geopolymers

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HIGHLIGHTS

- Alkali activated slag and geopolymers were synthesized for pervious concrete.
- Ambient cured clinker-free alkali activated materials were used.
- Alkali activated materials are suited for the in-situ production of pervious concrete.
- Better mechanical properties and water permeability than those of cement were reached.
- Metakaolin-slag geopolymer showed best mechanical properties and water permeability.

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ABSTRACT

In this paper, clinker-free cementitious binders were synthesized to produce ambient temperature cured pervious concrete of high aggregate-to-binder ratio. The binders are alkali activated slag, metakaolin geopolymer and metakaolin-slag geopolymer. Effects of aggregate size and binder type on the physical properties of resultant pervious concrete were studied in terms of compressive strength, density, total porosity and water permeability. Reaction products of binding materials were measured using X-ray diffraction (XRD) to study the reaction mechanisms. The pervious concretes produced in this work are not only environmentally friendly, but also achieved better mechanical properties and water permeability than cement pervious concretes.

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1. Introduction

Pervious concrete, also known as permeable concrete, is a special type of concrete with high porosity used for concrete flatwork [1]. The carefully controlled amount of cement paste, which in some cases contains supplementary cementitious materials (SCM) and chemical admixtures, plays the role of coating and binding the aggregate together [2]. Unlike conventional concrete, aggregates used for pervious concrete are normally of uniform particle size or have a narrow particle size distribution [1–3]. Due to the limited quantity or absence of fine aggregate, substantial amount of interconnected macro-pores are formed in this concrete system [4,5]. Generally, the porosity of pervious concrete is in the range of 15% to 35% by volume [1]. Studies have demonstrated that pervious concrete pavement possesses environmental benefits of decreasing storm water runoff, reducing the Urban Heat Island (UHI) effect, removing water pollutants, maintaining groundwater levels, etc [6–8]. All these make pervious concrete an eco-friendly

strategy for the low-impact development of pavements [9]. Field investigations of sidewalks, parking lots, recreation squares constructed using pervious concrete have been conducted in many countries [6]. The high porosity content of pervious concrete contributes to water infiltration, but results in significant decrease in mechanical strength [1,6]. As summarized by many authors [1,10], the typical water permeability of cement pervious concrete is 2–12 mm/s, while the corresponding compressive strength varies in the range of 25–5 MPa. To date, increasing attention has been drawn from academic and industrial fields to balance the water permeability and mechanical strength of pervious concrete products.

The general aggregate-to-binder ratio of cement based pervious concrete is in the range of 4–6 by mass [1]. Studies have demonstrated that increasing the aggregate-to-binder ratio results in the significant decrease in both compressive strength and static elastic moduli of the resulting pervious concrete [11,12]. Ghafouri and Dutta reported that aggregate gradation has significant influence on the properties of pervious concrete [13]. The addition of fine aggregate not only contributes to increase mechanical strength, but also improves the freeze-thaw resistance of resultant products [14,15]. Kevern [16] stated that the freeze-thaw deterio-

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ration of pervious cement concrete is directly related to aggregate type. Recently, polymers have been used to modify the performance of pervious concrete. Studies have shown that polymer fibers are helpful in increasing permeability, improving tensile strength, or enhancing the freeze-thaw resistance of cement pervious concrete [17,18]. However, special attention should be paid on the selection of polymer, since some macro-synthetic fibers, for example polypropylene, were reported to reduce the permeability of resulting pervious concrete [19].

The main part of the ecological footprint of pervious concrete results from the use of ordinary Portland cement (OPC). Statistical results show that over 3000 MJ of energy is consumed to produce one ton of cement even using the best available techniques (BAT) in Europe [20]. The worldwide average CO₂ emission is approximately 0.82 kg of per kg cement, making the cement industry accounts for around 5% of global CO₂ emissions [20,21].

Over the years, efforts have been made in reducing the greenhouse gas emission for sustainable development of road. Reducing the consumption of cement clinker by blending SCMs is one of the effective practices. Yang and Jiang [22] revealed that the addition of silica fume in cement pervious concrete could obviously enhance its strength. In addition, the combination of silica fume and superplasticizer had synergistic effect on improving the abrasion resistance of pervious concrete [22]. A ternary cementitious system containing cement, slag and fly ash provided a better workability, higher strength and a better long-term performance than its OPC counterpart [23,24].

To better meet the sustainable development of pavement, work has been ongoing in looking for clinker-free cementitious binders. Alkali activated materials (AAM) are among the most widely researched alternative binders for construction. The alkali activation system is generally classified into alkali activated slag (AAS) and geopolymers, depending on the chemistry of structure dominating gels. The main reaction product of AAS is calcium aluminosilicate hydrates (C-A-S-H) gel [21,25]. C-A-S-H differs from C-S-H (main product of OPC hydration) in chemical composition and structure, since the penetrated Al³⁺ mainly exists in tetrahedral bridging sites within the silicate chains of C-A-S-H [25]. In contrast, the alkali activation of metakaolin (MK) and siliceous fly ash (FA) forms geopolymers, which is composed of highly cross-linked, structurally disordered aluminosilicate gels (N-A-S-H) [26,27]. In contrast to C-A-S-H, the geopolymer is poor in calcium [21]. Though they lack long-range crystalline order, geopolymers are reported to share the nanostructural features of zeolites in chemical sense [21]. By investigating the coordination of silicon and aluminium geopolymer, Duxson et al. [28] reported that substitution of silicon by aluminium takes place inside the gel framework and the associated negative charge is balanced by alkali cations. In spite of the differences in composition and nanostructure between C-A-S-H and N-A-S-H, both gels are estimated to possess excellent mechanical and physicochemical durability properties [28,29]. Therefore, superior mechanical properties to traditional cementitious binders are certainly achievable by AAM under well-designed synthesis procedure [29]. In addition, AAM is reported to be environmentally friendly because it can reduce CO₂ emission by 9–97% in comparison with OPC [21].

Environmentally friendly pervious concretes have been developed using FA geopolymer as binder [30–32]. According to Tho-

in et al. acceptable compressive strengths of 8.4–11.4 MPa were obtained even increasing the aggregate-to-binder mass ratio to 8 [30]. In a study conducted by Sata et al. [32], effect of aggregate type on performance of FA geopolymer pervious concrete was investigated. FA geopolymer pervious concrete manufactured using natural coarse aggregate achieved the highest mechanical strength, while those made using recycled aggregate from crushed structure concrete had the best water permeability. However, due to the low reactivity of FA, pervious concrete produced using FA based geopolymer normally require curing at elevated temperatures. This brings difficulty to the in-situ application of FA geopolymer pervious concrete.

In this work, ambient cured binders, i.e. AAS using ground-granulated blast furnace slag (GGBS) as solid precursor, MK geopolymer (MKG) and MK-GGBS geopolymer (MGG), were synthesized. To test the suitability of these binders for the production of superior pervious concrete, a high aggregate-to-binder ratio was used. Effects of aggregate size on the compressive strength, density, total porosity and water permeability of resultant pervious concrete were studied. Properties of pervious concretes produced using different binders were compared. Reaction products of AAS, MKG and MGG were analysed using X-ray diffraction (XRD) to study the reaction mechanism. The results of this work might be valuable for the development of sustainable pervious concrete.

2. Materials and methods

2.1. Materials

Commercially available MK and GGBS were used in this study. The bulk chemical compositions were determined using X-ray fluorescence and are listed in Table 1. The Blaine specific surface area value of MK and GGBS were 5397 cm²/g and 4224 cm²/g, respectively.

Powder XRD measurement was applied to study the mineral composition of MK and GGBS, the obtained data were then quantitatively analysed using Rietveld refinement method (details about the measurement are given in section 2.5 and quantification method can be found in [33,34]). The XRD patterns of MK and GGBS are shown in Fig. 1, and the quantitative results are listed in Table 2.

Our previous study [34] has demonstrated that mainly the amorphous phase in MK and GGBS undergo geopolymerization. Zhang et al. [35] recommended to use the composition of amorphous phases to assess the suitability of solid precursors for AAM synthesis. Chemical compositions of amorphous phases in MK and GGBS were obtained by subtracting the mineral components from the bulk composition and are shown in Table 3.

NaOH solution of 9 mol/L and commercial sodium silicate solution (Na₂O(SiO₂)_n·xH₂O, containing 23.7 wt% SiO₂, 16.4 wt% Na₂O and 59.9 wt% H₂O, with a SiO₂/Na₂O molar ratio of 1.5) were used as alkali activators in this work. Analytical grade NaOH pellets were first dissolved in deionized water, and stored in an airtight container for at least 24 h prior to use for cooling down to room temperature.

Three sets of binders were synthesized for the manufacture of pervious concrete. The oxide molar ratios of each set are listed in Table 4. The oxide molar ratios were calculated based on the chem-

Table 1
Bulk chemical composition of MK and GGBS, given in % by weight.

	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	MgO	P ₂ O ₅	TiO ₂	MnO	Na ₂ O	K ₂ O	Sulfur ^a	Sulfide	LOI ^b
MK	32.58	61.24	0.13	1.17	0.15	0.05	1.64	n.d. ^c	0.17	0.63	0.07	n.d. ^c	1.76
GGBS	10.53	40.28	34.54	0.39	8.63	0.15	0.40	1.14	0.59	1.62	2.19	0.71	0.47 ^d

a, sulfur as SO₃; b, loss on ignition up to 950 °C; c, non-detected; d, tested in protective gas atmosphere.

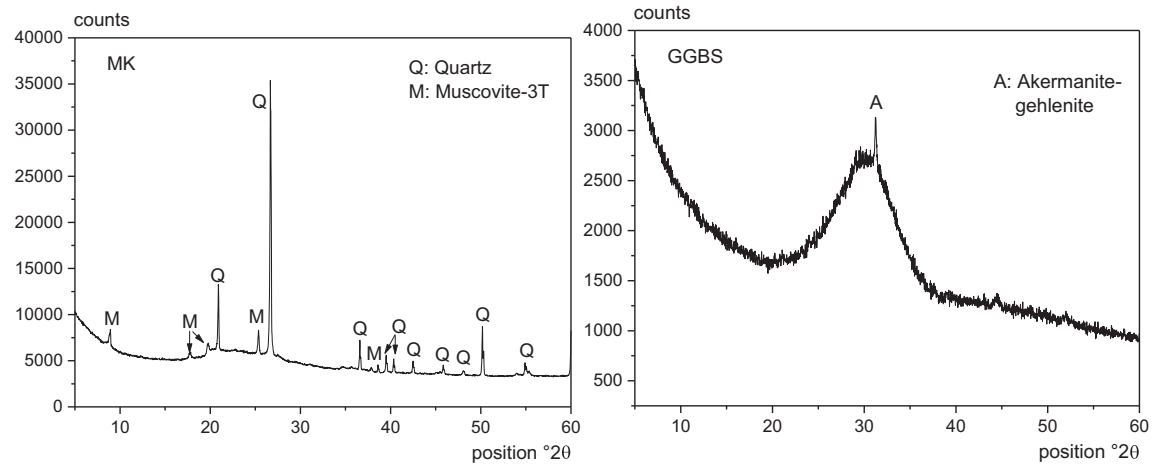


Fig. 1. XRD pattern of MK and GGBS.

Table 2

Mineralogical composition of MK and GGBS, given in % by weight [34].

Phase	PDF-Nr.	MK	GGBS
Quartz	98-002-3071	12.5	–
Muscovite 3T	98-003-4922	3.3	–
Akermanite-Gehlenite	98-011-3072	–	5.1
Amorphous	–	84.2	94.9

ical composition of amorphous phases shown in Table 3, which represents the ratios of reactive components in the reaction system. The CaO content is the highest in the AAS system, while MKG and MGG comprise similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Na}_2\text{O}$ ratios.

The liquid-to-solid ratio was 0.38, 0.6 and 0.4 for AAS, MKG and MGG, respectively. These values were determined based on pre-tests. Table 5 shows the mix proportions of the pervious concretes produced in this work. Coarse aggregates used were natural gravel of three sizes, 2–4 mm, 4–8 mm and 8–16 mm. To study the effect of aggregate size on the properties of AAS, MKG and MGG pervious concrete, the aggregate-to-binder ratio of 8 was kept constant throughout this work and each aggregate was separately mixed with three different binding materials. In total, 9 groups of pervious concrete were made.

2.2. Sample preparation

Weighted precursors and activator were mixed for 5 min in mechanical mixer to obtain a homogeneous blend. Aggregate was then added and further mixed for another 5 min. The Mixture was molded and tamped for compaction. For each group, cubes with a side length of 150 mm were made for compressive strength measurement, and cylindrical samples with a diameter of 100 mm and 200 mm height were produced for density, porosity and permeability study. All samples were covered with polyethylene (PE) foil and cured at 20 °C with 95% relative humidity. After 24 h, the samples were demolded, sealed using PE foil and transferred to a curing room of 20 °C and 65% relative humidity prior to test.

Table 3

Calculated chemical composition of the amorphous phase in MK and GGBS, given in % by weight [34].

	Al_2O_3	SiO_2	CaO	Fe_2O_3	MgO	TiO_2	MnO	Na_2O	K_2O	Others
MK	31.7	47.1	0.1	1.0	0.1	1.6	–	0.2	0.3	2.2
GGBS	9.6	38.5	32.4	0.4	8.2	0.4	1.1	0.6	1.6	2.0

2.3. Strength, density and total porosity measurement

After curing for 7 d, compressive strength was measured. The force was applied at a rate of 9 kN/s. The bulk density is calculated by dividing the weight of sample by the respective volume. Sample dimensions were measured using a caliper, average length to the nearest 0.25 mm was recorded. The total porosity was determined following ASTM C1754 [36]. Considering that high temperature drying may cause change in the crystal structure and even cracks within the specimen. The moderate temperature (40 °C) drying procedure in ASTM C1754 was applied to measure the dry weight. The dried samples were then submerged in water bath for the measurement of weight under water. The total porosity can then be calculated using Eq. (1) [37]. The results shown in this paper are the average values of three samples.

$$P = \left(1 - \left(\frac{w_2 - w_1}{\text{Vol} \cdot \rho_w} \right) \right) \cdot 100 \quad (1)$$

P total porosity, %

w_1 sample weight under water, g

w_2 dry weight, g

Vol sample volume, mm^3

ρ_w water density at measuring temperature, g/mm^3 .

2.4. Water permeability measurement

One of the key parameters of pervious concrete is its water permeability. The permeability coefficient of AAS and geopolymer pervious concretes were measured using the constant water head method. As shown in Fig. 2, the lateral surface of cylindrical specimen was tightly covered using rubber cuff to prevent water leakage. Permeated water was collected when constant water head was reached. Permeability coefficient was calculated according to Eq. (2) [37]. Average result of three measurements was reported.

$$k = \frac{QL}{HAt} \quad (2)$$

Table 4

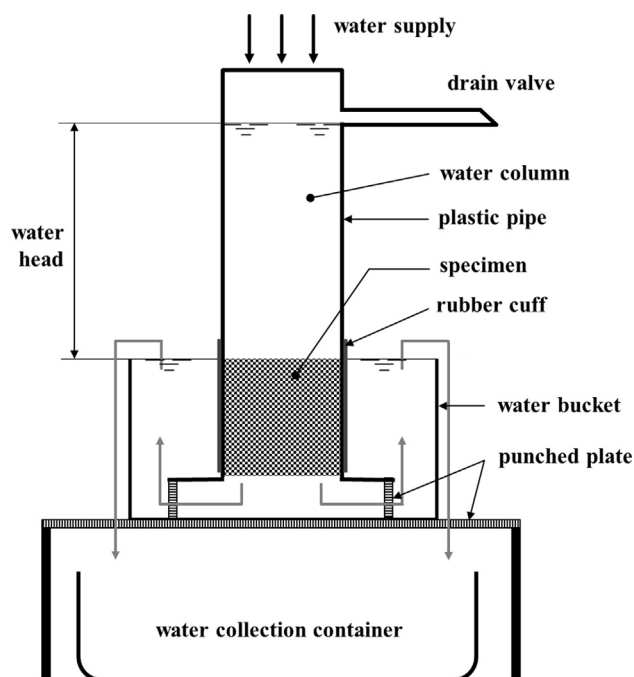
Oxide molar ratio of AAS, MKG and MGG binders.

Binder	SiO ₂ /Al ₂ O ₃	SiO ₂ /Na ₂ O	SiO ₂ /(Na ₂ O + CaO)	CaO/(SiO ₂ + Al ₂ O ₃)
AAS	8.829	4.249	1.073	0.625
MKG	2.617	6.273	6.187	0.002
MGG	2.944	5.585	3.051	0.111

Table 5

Mix proportions of AAS, MKG and MGG pervious concrete.

	MK kg	GGBS kg	NaOH solution kg	Sodium silicate solution kg	Aggregate kg	Aggregate size mm
AAS1	0	1.40	0.43	0.10	11.20	2–4
AAS2	0	1.40	0.43	0.10	11.20	4–8
AAS3	0	1.40	0.43	0.10	11.20	8–16
MKG1	1.40	0	0.17	0.67	11.20	2–4
MKG2	1.40	0	0.17	0.67	11.20	4–8
MKG3	1.40	0	0.17	0.67	11.20	8–16
MGG1	1.12	0.28	0.45	0.11	11.20	2–4
MGG2	1.12	0.28	0.45	0.11	11.20	4–8
MGG3	1.12	0.28	0.45	0.11	11.20	8–16

**Fig. 2.** Schematic diagram of water permeability measurement [38].

k water permeability, cm/s

Q quantity of water collected, m³

L specimen length, cm

H water head, cm

A cross sectional area of tested specimen, cm²

t time of water collection, s.

crushed to pass 1 mm sieve. Crushed particles were mixed with 100 ml isopropanol for 15 min to stop reactions. Mixture was then filtered and rinsed using isopropanol and diethyl ether, followed by being dried at 40 °C and manually ground using agate mortar to pass through 63 μm. Samples were stored in desiccator to prevent carbonation prior XRD measurement.

Cu Kα X-ray was generated under 40 kV and 40 mA tube operating conditions, data were collected over the 2 θ range of 5–60° in theta-theta geometry. XRD measurement of source precursors were operated using the same configuration. Obtained diffraction patterns were analyzed using the software HighScore Plus.

3. Results and discussion

3.1. Physical properties of AAS, MKG and MGG pervious concrete

High early age strength is important for the top layer of roads, in order to minimize traffic control and provide effective solution for early opening of traffic [23]. In addition, most published works paid attention to the early characteristics of pervious concrete. To better compare with literature [11,15,19,23,24,30–32], measurements conducted at 7 d are shown in this paper. Table 6 lists the compressive strength, density, porosity content and water permeability of AAS, MKG and MGG pervious concrete.

Comparing the effect of aggregate size within each set, similar conclusion can be drawn. Increasing aggregate size within the studied range lowers the compressive strength and density of resultant pervious concrete, while the total porosity and water permeability behaves in an opposite way. This can be assigned to the fact that smaller aggregate contributes to a more compact structure of concrete and improves the connecting interfaces between aggregate and binder [22].

It should be mentioned that pervious AAS, MKG and MGG concretes comprising 4–8 mm aggregate possess higher compressive strength than most reported cement pervious concretes [22,30–32,37], and the water permeability is sufficient to withstand cloud-burst or other extreme precipitations. Due to the similar porosity with literature listed in Table 7, the AAS2, MKG2 and MGG2 were selected for further comparison.

Comparing with the OPC system, better physical properties can be achieved by the binders developed in this work with high aggregate-to-binder ratio. In addition, no additive is needed in this work. All these contribute to reduce binder consumption and to

2.5. XRD measurement and data analysis

Mineralogical evolutions of the AAS, MKG and MGG were studied via powder XRD. Paste samples were made according to the mix design listed in Table 4, and cured under the same condition as the pervious concretes. After 7 d curing, 3 g of the pastes were

Table 6

Physical properties of AAS, MKG and MGG pervious concrete at an age of 7 d.

	Compressive Strength MPa	Density kg/m ³	Porosity %	Permeability cm/s
AAS1	20.3	2190	19.0 ± 1.1	0.32 ± 0.08
AAS2	14.5	1880	26.3 ± 0.9	1.21 ± 0.10
AAS3	11.3	1680	31.9 ± 1.3	1.35 ± 0.07
MKG1	27.9	2090	16.4 ± 1.0	0.31 ± 0.05
MKG2	18.9	1740	25.5 ± 1.2	0.75 ± 0.09
MKG3	16.3	1600	30.6 ± 1.5	1.40 ± 0.08
MGG1	36.2	2110	17.7 ± 1.2	0.41 ± 0.07
MGG2	25.5	1780	29.5 ± 1.1	1.51 ± 0.10
MGG3	21.6	1640	34.5 ± 1.5	1.62 ± 0.09

Table 7

Compressive strength and water permeability of different cementitious pervious concrete.

Binder	Aggregate size mm	Aggregate to binder ratio w/w	Compressive strength MPa	Total porosity %	Water permeability cm/s	Additive	Curing condition	Reference
OPC	2.36–9.75	4	15.6	26.9	1.07	Sand, PP ^a , superplasticiser	32 °C, 50% RH ^b	[19]
OPC	5–10	–	13.8	–	0.89	Sand	20 °C, 95% RH	[22]
OPC	2.36–19	4	16.5	28.0	0.45	Sand, PPS ^c fiber	22–25 °C, in water	[37]
OPC	2.36–19	4	18.3	25.0	0.45	Sand, glass fiber, RHA ^d		[37]
FA geopolymer	4.5–9.5	8	13.6	24.2	1.25	–	60 °C for 48 h, then 23 ± 2 °C, 50% RH	[32]
FA geopolymer	12.5–20	8	11.4	28.7	2.05	–		[30]
FA geopolymer	4.75–9.5	3.6	7.6	33.7	0.6	–	90 °C for 48 h, then 25 °C	[31]
AAS	4–8	8	14.1	26.3 ± 0.9	1.21 ± 0.10	–	20 °C, 100% RH for 24 h, then 20 °C, 65% RH	This work
MKG	4–8	8	18.9	25.5 ± 1.2	0.75 ± 0.09	–		
MGG	4–8	8	25.5	29.5 ± 1.1	1.51 ± 0.10	–		

a, polypropylene; b, relative humidity; c, polyphenylene sulphide; d, rice husk ash.

simplify the in-situ production processes. To date, only a limited amount of work has been done in probing geopolymer as binder for pervious concrete [30–32]. Geopolymer synthesized in these pilot works were first cured at 60–120 °C for 48 h to enhance mechanical properties of resultant products. This significantly retards the possibility of in-situ application of FA geopolymer based pervious concrete. In addition, the materials manufactured in this work simultaneously possess high compressive strength and good water permeability. All these make the AAS, MKG and MGG pervious concrete more competitive.

With regard to the effect of binders, the MGG based pervious concrete showed higher compressive strength than those made from MKG and AAS using the same aggregate. The corresponding porosity and permeability of MGG are also higher. This is partially attributed to the excellent binding property of MGG derived from its physiochemical properties of the nano gels, which will be fully discussed in Section 3.3.

3.2. Correlation within physical properties of AAS, MKG and MGG pervious concrete

Fig. 3 shows the relationship of total porosity and compressive strength, total porosity and water permeability. In Fig. 3(a), by performing linear regression, a satisfactory trend between total porosity and compressive strength within each set of pervious concrete can be seen. Yang and Jiang [22] stated that the strength of interface between binder and aggregate is relatively weak. When subjected to loading, pervious concrete always fails in this interfacial zone. Low porosity, which represents increased connecting, contributes to the gain of strength.

Fig. 3(b) plots the total porosity and water permeability of AAS, MKG and MGG pervious concretes. A close to linear trend can be

inferred showing that the water permeability increases with the increase of total porosity. The variation can be assigned to that the porosity measurement cannot perfectly represent effective porosity contributing to the water permeability of pervious concrete. Though a harmonised standard method is used in this work [36], further modification for more precise characterization of the void property is needed.

3.3. Reaction products of AAS, MKG and MGG

The mineral composition was documented using XRD. Fig. 4 shows the patterns of AAS, MKG and MGG pastes. Comparing with the patterns of source precursors, crystalline phases initially contained in GGBS and MK are unlikely to undergo alkali activation.

The reaction process of AAS can be simplified as the dissolution of Ca, Si and Al from slag, followed by the reorientation, interaction and condensation of dissolved species [29,39,40]. The intensive reflections around 7°, 30° and 50° 2θ in AAS pattern represent formation of C-A-S-H, which is the predominant reaction products of AAS. Al³⁺ penetrated into the C-A-S-H chain is of tetrahedral coordination, while octahedral aluminium tends to form other reaction products. The peaks at 11.6°, 23.3°, 34.9° and 46.8° 2θ reflect the generation of secondary product, hydrotalcite ((Mg₄Al₂)(OH)₁₂(CO₃)(H₂O)₃)_{0.5}, PDF No. 98-000-6182). According to Wang and Scrivener [41], hydrotalcite possess a layer structure similar to brucite, in which the interlayer region contains CO₃²⁻ ions and water molecules.

Different from AAS, reaction process of geopolymer mainly comprises dissolution and gelation of Si and Al from precursors, condensation and polymerization of gels. Comparing the patterns of MKG with MK, though no crystal was dissolved or formed during geopolymerization, an obvious shift of the amorphous hump to

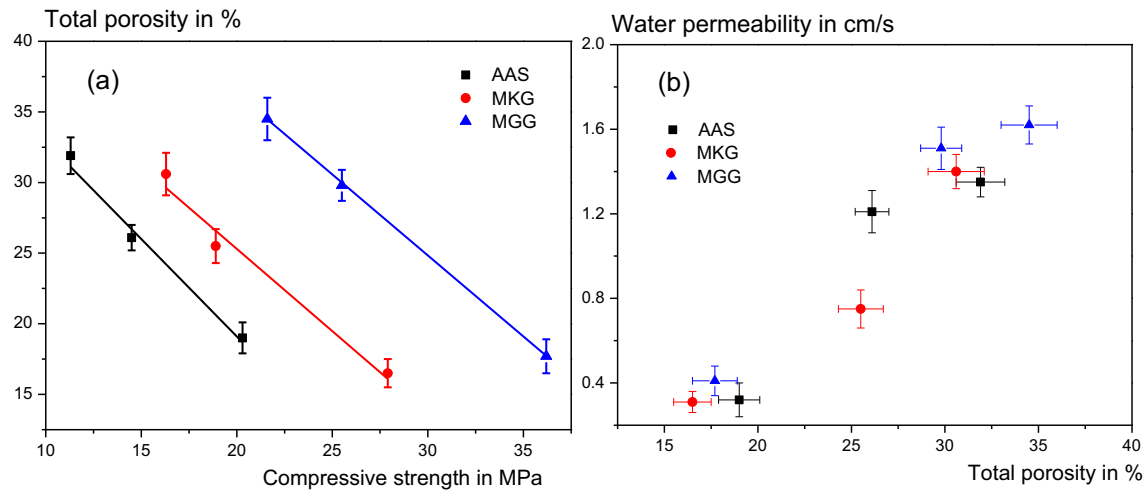


Fig. 3. Correlation of (a) total porosity-compressive strength and (b) total porosity-water permeability of AAS, MKG and MGG pervious concrete.

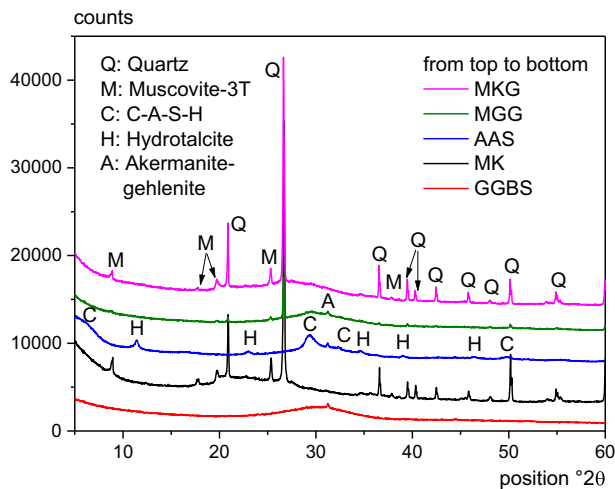


Fig. 4. XRD patterns of AAS, MKG and MGG pastes.

higher 2θ angles can be identified. This is an indication of the formation of amorphous geopolymeric structure [21].

In the XRD pattern of MGG, The quartz, muscovite and akermanite-gehlenite in the XRD pattern of MGG are the unreacted mineral from solid precursors. The broad hump centring around 20–40° 2θ is composed of semi-crystalline C-A-S-H and structurally disordered N-A-S-H. The coexistence of C-A-S-H and N-A-S-H was first reported by Yip et al. [42], by investigating the alkali activation of MK-GGBS mixture. Yip et al. [42] stated that simultaneous formation of C-A-S-H and N-A-S-H contributes to bridge the gaps among different phases and unreacted particles, resulting in the superior mechanical properties of MK-GGBS geopolymer. This well explains the higher compressive strength of MGG pervious concrete compared to AAS and MKG.

4. Conclusion and outlook

In this work, ambient cured AAS, MKG and MGG binders were synthesized for the production of pervious concrete. Effects of aggregate size on the compressive strength, bulk density, total porosity and water permeability were studied. Reaction products of each binder was analysed using XRD. Following conclusions can be drawn:

- (1) Increasing aggregate size within the studied range in this work increases the total porosity and water permeability of resulting pervious concrete, but lowers the compressive strength and density.
- (2) Pervious concrete made from MGG achieved the highest compressive strength, followed by MKG and AAS using aggregate of the same size. All these three binding materials are superior to typical cement binder.
- (3) The main reaction products of AAS and MKG are C-A-S-H and N-A-S-H gels, respectively. Coexistence of both gels was found in MGG, which contributes to the better performance of MGG pervious concrete.

The authors are aware that though the synthesized AAS, MKG and MGG binders are suited for the in-situ production of pervious concrete, further work is required to optimize the AAM pervious concrete system. Future work will more comprehensively study the effects of different production parameters, as well as the stability and durability of resultant pervious concrete. Also the environmental and economic advantages will be evaluated in detail. Results obtained from this series of studies will contribute to the sustainable development of pervious concrete.

Conflict of Interest

None.

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